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XXII. *The Stresses in a Wire Wheel with non-Radial Spokes under Loads applied to the Rim.*

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IT has been shown in an earlier paper † that the stresses in a radially spoked wire wheel caused by a radial load on the rim can be obtained with considerable accuracy from a consideration of the case of a wheel having an infinite number of spokes. In the present paper a similar treatment is applied to the general problem of the wire wheel in which the spokes, instead of being radial, fall into two systems, those of one system being inclined at a constant angle to the radius, and those of the second at the same angle to the other side of the radius. Two arrangements are shown in fig. 1.

Such a wheel differs from the radially spoked type in that it can resist, not only radial loads, but those in any direction in the plane of the wheel. Solutions are therefore given for the stresses under radial and tangential rim loads acting separately; superposition of these solutions enables the stresses to be calculated when the load acts in any direction.

Following the process of the former analysis it will be supposed that a rim is connected to a rigid hub by two disks,

* Communicated by the Authors.

† "The Stresses in a Radially-spoked Wire Wheel under Loads applied to the Rim," A. J. Sutton Pippard and W. E. Francis, Phil. Mag. xi. pp. 233-285 (Feb. 1931).

each of which has the property of transmitting stress in one direction only : one along lines inclined at an angle ϵ to the radius, the other along lines inclined at $-\epsilon$, as shown in fig. 2. Further, the stress along any such line is to be constant, so that the disks vary in thickness from the hub to the rim.

Fig. 1.

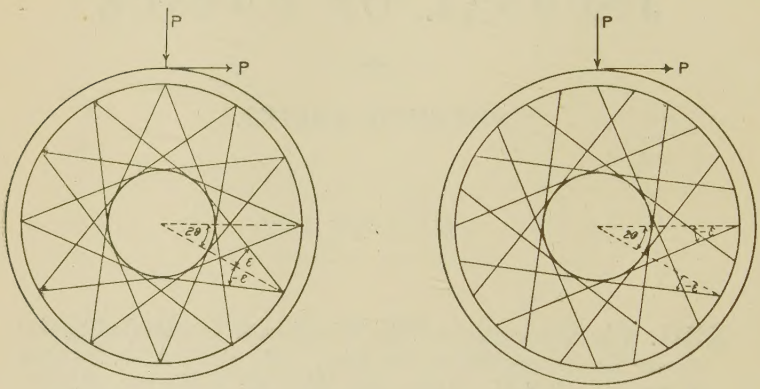
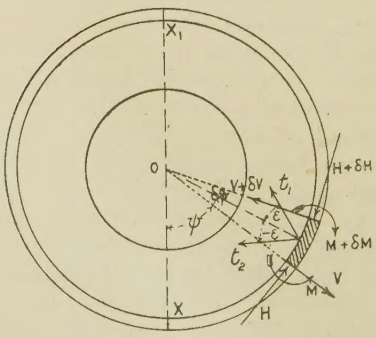


Fig. 2.



Let R be the radius to the centroid of the rim,

R_0 the radius to the tangent circle on the hub,

I the moment of inertia of the cross-section of the rim about its axis of bending,

a the cross-sectional area of the rim,

E_1 the modulus of elasticity of the rim material,

E_2 the modulus of elasticity of the disk material,

t_1 the inward pull per unit length of rim of the disk acting at ϵ to the radius,

t_2 the inward pull per unit length of rim of the disk acting at $-\epsilon$ to the radius.

At any point on the rim at an angular distance ψ from XO in fig. 2,

let u be the outward radial movement,

and v the counterclockwise tangential movement.

Also let H be the tangential force on the rim at this point,

V the radial force,

and M the bending moment,

the positive directions of these being as shown in the figure. Then we have *

$$H = -\frac{E_1 a}{R}\left(u + \frac{\partial v}{\partial \psi}\right) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$M = \frac{E_1 I_1}{R^2}\left(u + \frac{\partial^2 u}{\partial \psi^2}\right) . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

By resolution of the forces acting on a small element of the ring as shown in the figure, we obtain

$$\frac{\partial H}{\partial \psi} = -V + R(t_1 - t_2)\sin\epsilon \quad . \quad . \quad . \quad . \quad (3)$$

$$\frac{\partial V}{\partial \psi} = H - R(t_1 + t_2)\cos\epsilon \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\frac{\partial M}{\partial \psi} = VR, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and these equations lead to

$$\frac{\partial^5 u}{\partial \psi^5} + 2\frac{\partial^3 u}{\partial \psi^3} + \frac{\partial u}{\partial \psi} + \frac{R^4}{E_1 I}\left\{\frac{\partial}{\partial \psi}(t_1 + t_2)\cos\epsilon - (t_1 - t_2)\sin\epsilon\right\} = 0. \quad (6)$$

If the thickness of each disk at the rim is Δ, we have

$$\left.\begin{aligned} t_1 &= \frac{E_2 \Delta}{R}(u - v\tan\epsilon) \\ t_2 &= \frac{E_2 \Delta}{R}(u + v\tan\epsilon) \end{aligned}\right\}, \quad . \quad . \quad . \quad (7)$$

* 'Dynamical Theory of Sound,' H. Lamb, 2nd ed. p. 135.

and equation (6) becomes

$$\frac{\partial^5 u}{\partial \psi^5} + 2\frac{\partial^3 u}{\partial \psi^3} + \frac{\partial u}{\partial \psi} + \frac{2E_2 \Delta R^3}{E_1 I}\left(\frac{\partial u}{\partial \psi}\cos\epsilon + v\sin\epsilon\tan\epsilon\right) = 0. \quad . \quad (8)$$

As in the previous analysis it will be assumed that $1/\alpha E_1$ is negligible compared with $R^2/E_1 I$, so that for H to be finite, we have from equation (1),

$$u = -\frac{\partial v}{\partial \psi}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Differentiating equation (8) with respect to ψ, and substituting this relationship, we obtain

$$\frac{\partial^6 u}{\partial \psi^6} + 2\frac{\partial^4 u}{\partial \psi^4} + (1 + K_1\cos\epsilon)\frac{\partial^2 u}{\partial \psi^2} - K_1 u\sin\epsilon\tan\epsilon = 0,$$

where $$K_1 = \frac{2\Delta E_2 R^3}{E_1 I}.$$

The complete solution of this equation is

$$u = A\sinh\gamma\psi + B\cos\alpha\psi\sinh\beta\psi + C\sin\alpha\psi\cosh\beta\psi + D\cosh\gamma\psi + E\cos\alpha\psi\cosh\beta\psi + F\sin\alpha\psi\sinh\beta\psi. \quad (10)$$

where

$$\left.\begin{aligned}
\alpha &= \sqrt{\frac{\left(\frac{X^2}{4} + \frac{2X}{3} + \frac{4}{9} + \frac{3Y^2}{4}\right)^{\frac{1}{2}} + \left(\frac{X}{2} + \frac{2}{3}\right)}{2}}, \\
\beta &= \sqrt{\frac{\left(\frac{X^2}{4} + \frac{2X}{3} + \frac{4}{9} + \frac{3Y^2}{4}\right)^{\frac{1}{2}} - \left(\frac{X}{2} + \frac{2}{3}\right)}{2}}, \\
\gamma &= (X - 2/3)^{\frac{1}{2}}, \\
X &= (M+Q)^{\frac{1}{3}} + (M-Q)^{\frac{1}{3}}, \\
Y &= (M+Q)^{\frac{1}{3}} - (M-Q)^{\frac{1}{3}}, \\
M &= \frac{1}{27} + \frac{K_1\sec\epsilon}{6}(2 + \sin^2\epsilon), \\
Q &= \sqrt{\frac{K_1}{27}\left[K_1^2\cos^3\epsilon + K_1\left\{2 + \sin^2\epsilon\left(7 + \frac{27}{4}\tan^2\epsilon\right)\right\} + \sec\epsilon\right]}.
\end{aligned}\right\} \quad . \quad (11)$$

In the analysis for the radially spoked wheel

$$K=\frac{\Delta_1 E_2}{L}\cdot\frac{R^4}{E_1 I},$$

where Δ_1 is the thickness of the single disk connecting the rim and hub, and L is the length of a spoke.

Hence
$$\frac{K_1}{K}=\frac{2\Delta L}{R\Delta_1}.$$

Since 2Δ is the total thickness of the connecting disks in the present case, and L becomes $R\cos\epsilon$, we have

$$K_1=K\cos\epsilon.$$

In the limit when $\epsilon=0$, γ is zero, and α and β reduce to the values obtained for the radially spoked wheel, viz.:

$$\alpha_0=\sqrt{\tfrac{1}{2}\{(K+1)^{\frac{1}{2}}+1\}},$$
$$\beta_0=\sqrt{\tfrac{1}{2}\{(K+1)^{\frac{1}{2}}-1\}}.$$

Case I.—Radial Load acting on the Rim.

Let a radial load P act inward on the rim at X_1, diametrically opposite the origin (figs. 1 and 2). From considerations of symmetry it is clear that the values of u are equal for equal positive and negative values of ψ, and so the constants A, B, and C in equation (10) are all zero. The solution for this case is therefore

$$u=D\cosh\gamma\psi+E\cos\alpha\psi\cosh\beta\psi+F\sin\alpha\psi\sinh\beta\psi, \quad (12)$$

$$v=-\left[\frac{D}{\gamma}\sinh\gamma\psi+\frac{E\beta-F\alpha}{\alpha^2+\beta^2}\cos\alpha\psi\sinh\beta\psi + \frac{E\alpha+F\beta}{\alpha^2+\beta^2}\sin\alpha\psi\cosh\beta\psi+H\right]. \quad (13)$$

Since $v=0$ when $\psi=0$, $H=0$.

To determine the constants D, E, and F, the following conditions are used:

When $\psi=\pi$, $v=0$.

When $\psi=\pi$, $\frac{\partial u}{\partial\psi}=0$.

The total vertical force on the rim is zero, or

$$4\Delta E_2\left[\cos\epsilon\int_0^\pi u\cos\psi\,d\psi-\sin\epsilon\tan\epsilon\int_0^\pi v\sin\psi\,d\psi\right]=P.$$

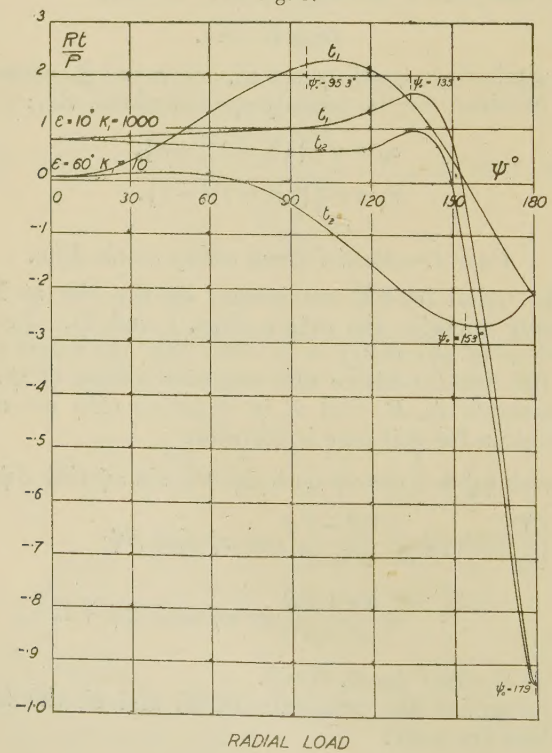
The remaining conditions for the static equilibrium of the rim are automatically satisfied. The constants are

$$D = Z\frac{2\alpha\beta\gamma}{\sinh\gamma\pi}$$

$$E = -Z\left\{\frac{\beta(\alpha^2+\beta^2-\gamma^2)\sin\alpha\pi\cosh\beta\pi+\alpha(\alpha^2+\beta^2+\gamma^2)\cos\alpha\pi\sinh\beta\pi}{\cosh^2\beta\pi-\cos^2\alpha\pi}\right\},$$

$$F = -Z\left\{\frac{\alpha(\alpha^2+\beta^2+\gamma^2)\sin\alpha\pi\cosh\beta\pi-\beta(\alpha^2+\beta^2-\gamma^2)\cos\alpha\pi\sinh\beta\pi}{\cosh^2\beta\pi-\cos^2\alpha\pi}\right\},$$

Fig. 3.



where $$Z = \frac{PK_1}{12\sqrt{3}\Delta E_2 Q}.$$

When $\epsilon=0$ these constants reduce to those previously found for the radially spoked wheel.

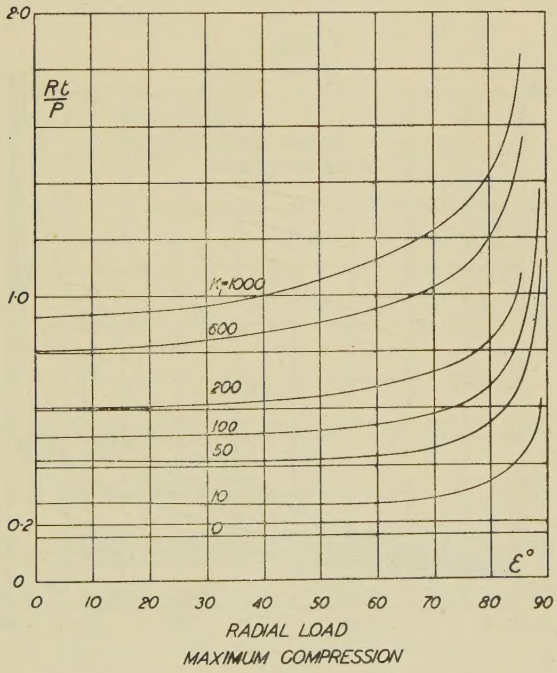
Values of u and v can now be calculated and the equations (7) then give t_1 and t_2. Typical curves showing the variation of these forces around the rim are given in fig. 3.

Maximum values of t_1 and t_2.—Reference to the curves of fig, 3 shows that the maximum compressive stress t_2 occurs at an angle ψ_0, which lies between the limits $\pi - \epsilon$ when K_1 is zero, and π when K_1 is infinite.

The maximum tensile stress t_1 lies between the limits ϵ when K_1 is zero, and π when K_1 is infinite.

Differentiation of the complete expressions for t_1 and t_2 do not lead to useful formulæ for the determination of the

Fig. 4.



positions of maximum values, but an approximation can be obtained by considering the periodic terms only. If these terms are differentiated and equated to zero, and if $\sinh \beta\psi_0$ is put equal to $\cosh \beta\psi_0$, which is very nearly true for all practical values of K_1, we obtain

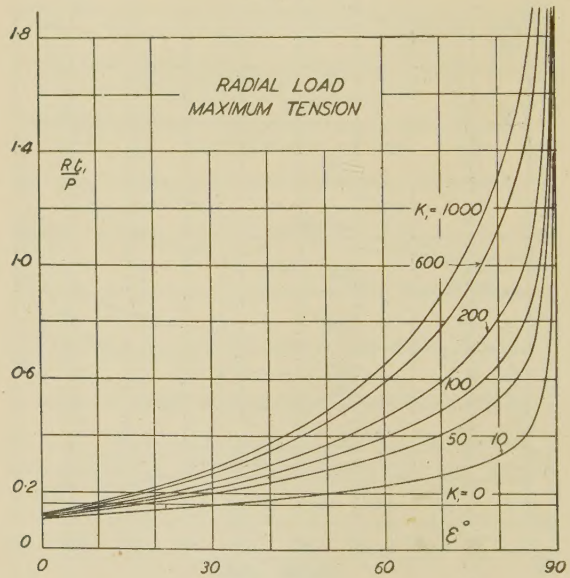
$$\tan \alpha\psi_0 = \frac{\alpha F + E(\beta \pm \tan \epsilon)}{\alpha E - F(\beta \pm \tan \epsilon)}, \quad \ldots \quad (14)$$

where the positive sign refers to t_1 and the negative sign to t_2.

The values of ψ_0 obtained from equation (14) are shown on the curves of fig. 3, and it will be seen that they are within about 7° of the true positions. Plotting the curves around these approximate values then gives the true positions.

Figs. 4 and 5 give the curves of maximum compressive and tensile stresses respectively, while figs. 6 and 7 show the positions of these maxima. Tables I and II. give the values used in plotting figs. 4 and 5. Sufficient curves are given to allow cross plotting, so that a curve of maximum t against K_1 can be obtained for any value of ϵ.

Fig. 5



Maximum bending moment in the rim.—Using equation (2) the bending moment at any point in the rim is

$$M = \frac{E_1 I}{R^2}\,[D(\gamma^2+1)\cosh\gamma\psi + \{(\beta^2-\alpha^2+1)E+2\alpha\beta F\}\cos\alpha\psi\cosh\beta\psi + \{(\beta^2-\alpha^2+1)F-2\alpha\beta E\}\sin\alpha\psi\sinh\beta\psi]. \quad (15)$$

Typical bending moment diagrams are shown in fig. 8. The greatest value occurs under the load, and putting $\psi=\pi$ in equation (15), the maximum moment is given by

Fig. 6.

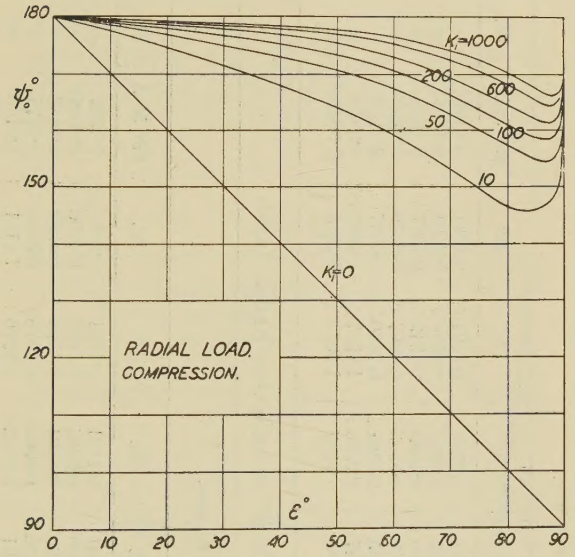

180
ψ°
150
120
90
0
10
20
30
40
50
60
70
80
90
ε°
K₁=1000
200
600
50
100
10
K₁=0
RADIAL LOAD.
COMPRESSION.

Fig. 7.

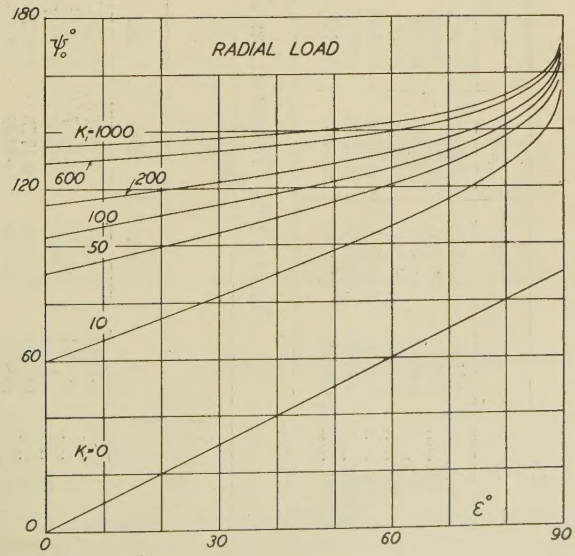

180
ψ°
120
60
0
0
30
60
90
ε°
RADIAL LOAD
K₁-1000
600
200
100
50
10
K₁-0

TABLE I.—Values of maximum Rt_2/P (compressive) for Radial Load.

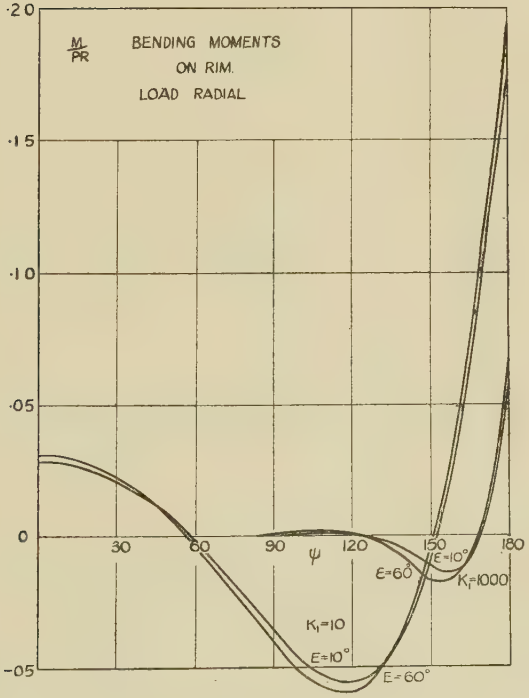
K_1.	ϵ degrees.									
	0.	10.	20.	30.	45.	60.	75.	85.	89° 59′.	90.
0	0·1591	0·1591	0·1591	0·1591	0·1591	0·1591	0·1591	0·1591	0·1591	—
10	0·2771	0·2760	0·2754	0·2695	0·2639	0·2663	0·3026	0·4108	2·4354	∞
50	0·4214	0·4212	0·4203	0·4197	0·4219	0·4360	0·4912	0·6627	4·1643	∞
100	0·5062	0·5058	0·5077	0·5091	0·5187	0·5415	0·6097	0·8270	5·2471	∞
200	0·6078	0·6091	0·6123	0·6193	0·6385	0·6761	0·7630	1·0247	6·6108	∞
600	0·8129	0·8156	0·8248	0·8416	0·8847	0·9585	1·0937	1·4625	9·5342	∞
1000	0·9299	0·9339	0·9468	0·9705	1·0283	1·1307	1·3073	1·7318	11·3049	∞

TABLE II.—Values of maximum Rt_1/P (tensile) for Radial Load.

K_1	ϵ degrees.									
	0	10.	20.	30.	45.	60.	75.	85.	89° 59′.	90.
0	0·1591	0·1591	0·1591	0·1591	0·1591	0·1591	0·1591	0·1591	0·1591	—
10	0·1061	0·1213	0·1397	0·1588	0·1900	0·2286	0·2927	0·4096	0·4354	∞
50	0·1108	0·1368	0·1662	0·1997	0·2600	0·3384	0·4594	0·6592	4·1643	∞
100	0·1129	0·1425	0·1773	0·2178	0·2932	0·3962	0·5578	0·8214	5·2471	∞
200	0·1160	0·1490	0·1892	0·2373	0·3301	0·4632	0·6793	1·0151	6·6108	∞
600	0·1231	0·1613	0·2092	0·2687	0·3947	0·5862	0·9244	1·4378	9·5342	∞
1000	0·1280	0·1675	0·2201	0·2859	0·4246	0·6500	1·0635	1·6963	11·3049	∞

$$\frac{M_0}{PR} = \frac{1}{6\sqrt{3}Q}\Bigg[2\alpha\beta\gamma(\gamma^2+1)\coth\gamma\pi$$
$$\frac{\alpha\sinh 2\beta\pi\{(\alpha^2+\beta^2)(\alpha^2+\beta^2-1)-\gamma^2(3\beta^2-\alpha^2+1)\}}{-\beta\sin 2\alpha\pi\{(\alpha^2+\beta^2)(\alpha^2+\beta^2+1)+\gamma^2(3\alpha^2-\beta^2-1)\}}\Bigg].$$
$$\cosh 2\beta\pi-\cos 2\alpha\pi \qquad \ldots \quad (16)$$

Fig. 8.



When K_1 is large, *i. e.*, for all practical wheels this reduces to

$$\frac{M_0}{PR} = \frac{\alpha}{6\sqrt{3}Q}[2\beta\gamma(\gamma^2+1)+(\alpha^2+\beta^2)(\alpha^2+\beta^2-1)$$
$$-\gamma^2(3\beta^2-\alpha^2+1)]. \quad (17)$$

Curves of maximum bending moment are shown in fig. 9, and the values from which these were plotted are given in Table III.

Fig. 9.

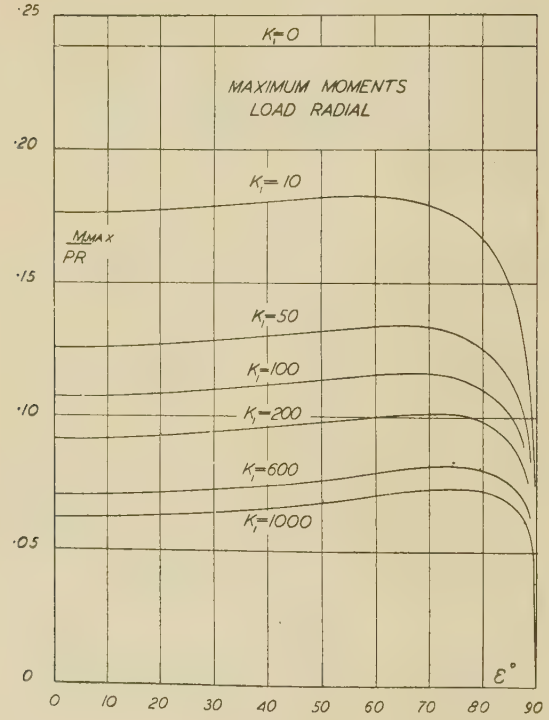


Table III.

Values of maximum M/PR for Radial Load.

K_1.	ϵ degrees.								
	0.	10.	20.	30.	45.	60.	75.	85.	90.
0 ...	0·2387	0·2387	0·2387	0·2387	0·2387	0·2387	0·2387	0·2387	—
10 ...	0·1762	0·1765	0·1773	0·1786	0·1809	0·1820	0·1747	0·1495	0
50 ...	0·1258	0·1261	0·1269	0·1283	0·1312	0·1337	0·1307	0·1143	0
100 ...	0·1075	0·1077	0·1085	0·1099	0·1128	0·1159	0·1150	0·1019	0
200 ...	0·0913	0·0916	0·0924	0·0937	0·0966	0·1001	0·1009	0·0902	0
600 ...	0·0702	0·0704	0·0711	0·0722	0·0749	0·0790	0·0815	0·0747	0
1000 ...	0·0620	0·0622	0·0628	0·0639	0·0664	0·0701	0·0735	0·0683	0

The accurate formula (16) has been used throughout. As before, sufficient curves are given to enable a curve of maximum M against K_1 to be plotted for any value of ϵ.

Case II.—Tangential Load acting on the Rim.

Let a tangential load P act at X_1 (figs. 1 and 2). Considerations of symmetry now show that for equal positive and negative values of ψ, the values of u are of equal magnitude but opposite in sign. Hence in equation (10) the constants D, E, and F must all be zero and the solution is

$$u = A \sinh \gamma\psi + B \cos \alpha\psi \sinh \beta\psi + C \sin \alpha\psi \cosh \beta\psi. \quad (18)$$

$$v = -\left[\frac{A}{\gamma}\cosh \gamma\psi + \frac{B\beta - C\alpha}{\alpha^2+\beta^2}\cos \alpha\psi \cosh \beta\psi + \frac{B\alpha + C\beta}{\alpha^2+\beta^2}\sin \alpha\psi \sinh \beta\psi + G\right]. \quad (19)$$

To determine the constants we use the conditions:

(*a*) When $\psi = \pi$, $\quad u = 0$.

(*b*) When $\psi = \pi$, the bending moment is zero, and as $u = 0$, therefore $\dfrac{\partial^2 u}{\partial \psi^2} = 0$ from equation (2).

(*c*) The total horizontal force on the rim is zero, *i. e.*

$$4\Delta E_2\left[\cos \epsilon \int_0^{\pi} u \sin \psi \, d\psi + \sin \epsilon \tan \epsilon \int_0^{\pi} v \cos \psi \, d\psi\right] = P.$$

(*d*) The total moment on the rim is zero. This leads to

$$4\Delta E_2 \sin \epsilon \tan \epsilon \int_0^{\pi} v \, . \, d\psi = -P.$$

The third condition of static equilibrium is automatically satisfied, and we obtain

$$A = Z\frac{2\alpha\beta}{\sinh \gamma\pi}.$$

$$B = -Z\left\{\frac{2\alpha\beta \cos \alpha\pi \sinh \beta\pi - (\alpha^2 - \beta^2 + \gamma^2)\sin \alpha\pi \cosh \beta\pi}{\cosh^2 \beta\pi - \cos^2 \alpha\pi}\right\}.$$

$$C = -Z\left\{\frac{(\alpha^2 - \beta^2 + \gamma^2)\cos \alpha\pi \sinh \beta\pi + 2\alpha\beta \sin \alpha\pi \cosh \beta\pi}{\cosh^2 \beta\pi - \cos^2 \alpha\pi}\right\}.$$

$$G = 0.$$

where Z has the same value as before.

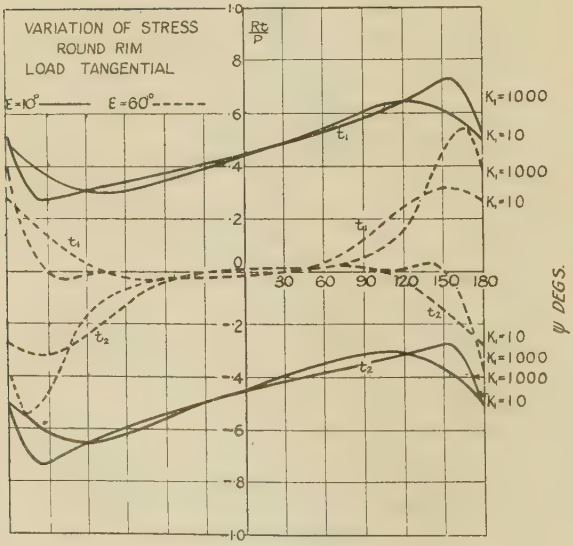
Relationships between constants.—These constants, A, B, and C, and those for the case when a radial load acts are connected by the following relationships:

$$A=\frac{D}{\gamma}, \qquad D=\gamma A,$$

$$B=\frac{E\beta-F\alpha}{\alpha^2+\beta^2}, \qquad E=B\beta+C\alpha,$$

$$C=\frac{E\alpha+F\beta}{\alpha^2+\beta^2}, \qquad F=C\beta-B\alpha,$$

Fig. 10.



and it follows that

$$v_r=-u_t,$$

$$\frac{\partial u_t}{\partial \psi}=u_r,$$

where the suffixes r and t denote values for a radial and a tangential load respectively. These relationships can be used to show that the maximum values of M and t under a tangential load occur when the corresponding actions under a radial load are zero. This point is shown in the curves of figs. 8 and 14 and those of figs. 3 and 10.

Table IV.

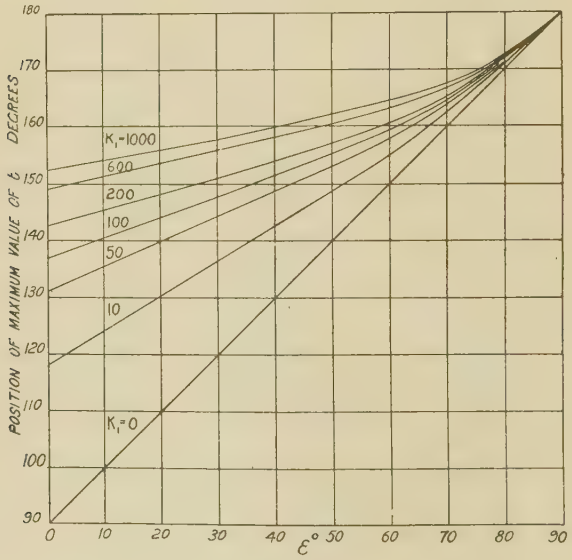
Values of maximum Rt/P (tensile and compressive) for Tangential Load.

K_1.	ϵ degrees.											
	0.	5.	10.	20.	30.	45.	60.	75.	85.	89° 54′.	89° 59′.	90.
0	∞	1·0722	0·6174	0·3918	0·3183	0·2717	0·2510	0·2460	0·2400	—	0·2387	—
10	∞	—	0·6483	0·4246	0·3600	0·3193	0·3197	0·3386	0·3933	—	0·9504	∞
50	∞	—	0·6708	0·4572	0·4021	0·3810	0·3907	0·4266	0·5003	—	1·2428	∞
100	∞	1·1253	0·6798	0·4739	0·4207	0·4063	0·4245	0·4740	0·5540	1·0348	1·3950	∞
200	∞	—	0·6913	0·4886	0·4396	0·4319	0·4602	0·5208	0·6212	1·1616	1·5658	∞
600	∞	—	0·7071	0·5092	0·4651	0·4720	0·5199	0·6107	0·7393	1·3950	1·8805	∞
1000	∞	1·1544	0·7294	0·5188	0·4788	0·4906	0·5485	0·6562	0·8025	1·5189	2·0475	∞

Maximum values of t_1 *and* t_2.—Equations (7), (18), and (19) can now be used to calculate t_1 and t_2, and the curves of fig. 10 show how these quantities vary around the rim. Differentiation of the expressions for t_1 and t_2 does not lead to a useful formula for determining the position at which maximum values occur, and positions must be found by plotting. Table IV. and fig. 12 give the magnitudes of the maximum stresses, and fig. 11 the position where they occur.

It should be noticed that the maximum compressive and tensile stresses in a wheel with a tangential load are equal in magnitude and occur at corresponding positive and

Fig. 11.



negative values of ψ, their lines of action being inclined at $\pm\epsilon$ respectively to the radii at these points. Fig. 13 shows a curve of maximum t plotted against K_1 for $\epsilon = 60°$, and similar curves for any value of ϵ can be obtained by cross plotting from fig. 12.

Maximum bending moment in the rim.—The bending moment in the rim at any point is, from equation (2),

$$M = \frac{E_1 I}{R^2}[A(\gamma^2+1)\sinh\gamma\psi + \{(\beta^2-\alpha^2+1)B + 2\alpha\beta C\}\cos\alpha\psi\sinh\beta\psi + \{(\beta^2-\alpha^2+1)C - 2\alpha\beta B\}\sin\alpha\psi\cosh\beta\psi]. \quad (20)$$

Fig. 12.

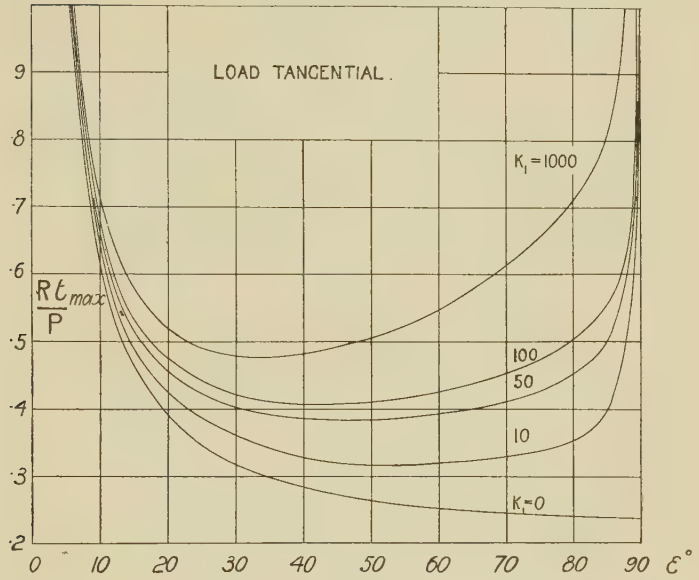
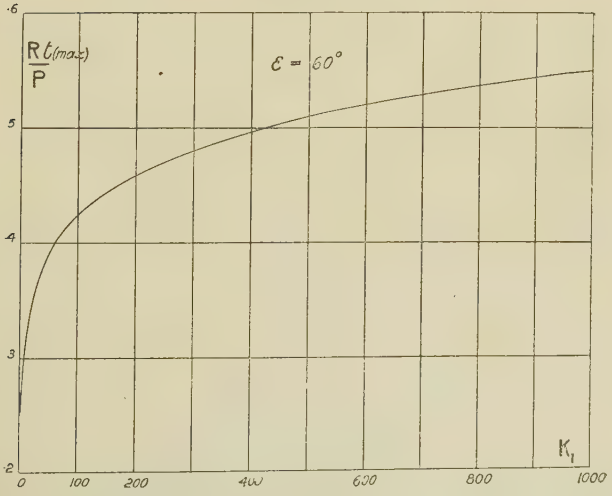

LOAD TANGENTIAL.
$K_1 = 1000$
100
50
10
$K_1 = 0$
$\frac{R t_{max}}{P}$
·9
·8
·7
·6
·5
·4
·3
·2
0
10
20
30
40
50
60
70
80
90
$\varepsilon°$

Fig. 13.


$\frac{R t_{(max.)}}{P}$
$\varepsilon = 60°$
·6
5
4
3
·2
0
100
200
400
600
800
1000
K_1

The curves of fig. 14 show typical bending moment diagrams for the rim and these indicate that the position of

Fig. 14.

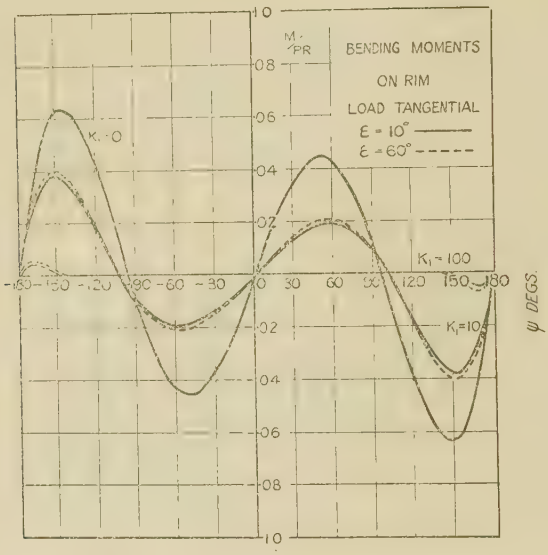
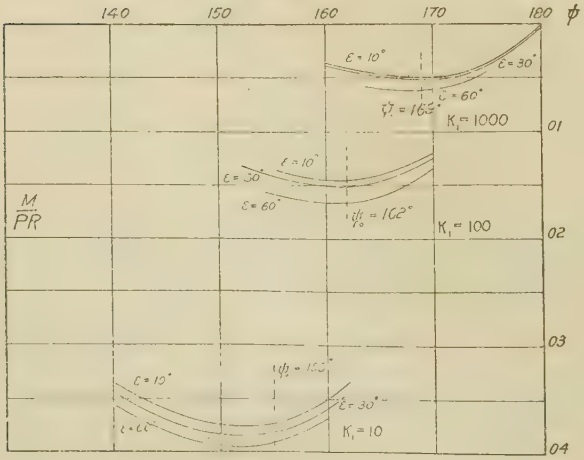


Fig. 15.

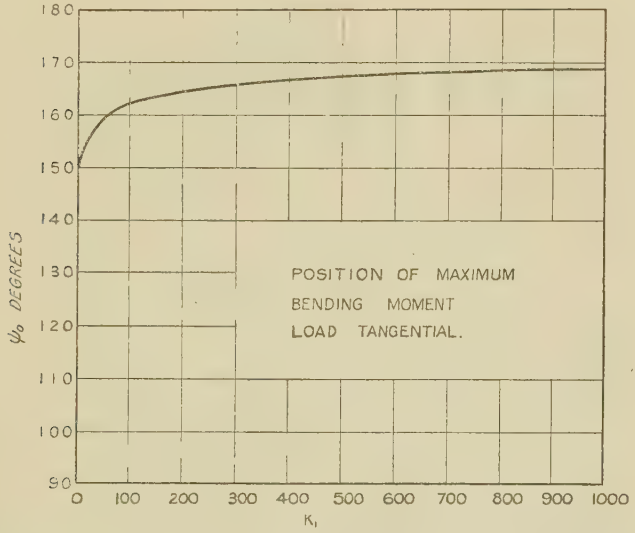


the maximum value is practically independent of ϵ, being controlled only by K_1. This point is further illustrated in

fig. 15, where the bending moment is plotted in the neighbourhood of the maximum for values of K_1 from 10 to 1000, and of ϵ from 10° to 60°. It appeared from this that a formula for the position of the maximum value based on the limiting case of $\epsilon=0$ would be reasonably accurate for all values of ϵ.

It was also found that this position was controlled by the periodic terms of equation (20) and that the omission of the first term introduced very little error, while making the resulting expression manageable. Since ψ is large for the value required, $\sinh \beta\psi$ can be put equal to $\cosh \beta\psi$ for all practical values of K_1.

Fig. 16.



Hence, differentiating the periodic terms of equation (20), putting $\sinh \beta\psi = \cosh \beta\psi$ and equating to zero, the position of the maximum bending moment is given by

$$\tan \alpha\psi_0 = \frac{B\beta(\beta^2-3\alpha^2+1)+C\alpha(3\beta^2-\alpha^2+1)}{B\alpha(3\beta^2-\alpha^2+1)-C\beta(\beta^2-3\alpha^2+1)} \quad . \quad (21)$$

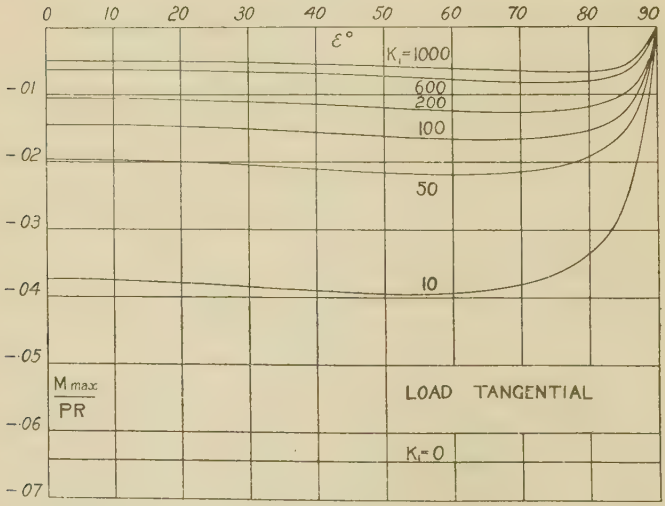
and in the limit when $\epsilon=0$, this becomes

$$\tan \alpha\psi_0 = \frac{\alpha_0 \sin \alpha_0\pi - \beta_0 \cos \alpha_0\pi}{\beta_0 \sin \alpha_0\pi + \alpha_0 \cos \alpha_0\pi}, \quad . \quad . \quad (22)$$

where ψ_0 is the position of maximum bending moment, and α_0 and β_0 are the values of α and β for the radially spoked wheel, as given earlier.

The values of ψ_0 calculated from this formula are shown on the curves of fig. 15, and for $K_1=100$ and $K_1=1000$ the agreement with actual values is good. As would be expected for $K_1=10$ the agreement is not quite so satisfactory, but this is outside the range of practical values. A curve of ψ_0 against K_1, defining the position of the maximum bending moment for a wide range of wheels is shown in fig. 16. For large values of K_1 this has been obtained by using equation (22) but for small values the accurate positions have been calculated. These values of ψ_0 substituted in equation (20) give the maximum bending moments

Fig. 17.



of Table V. from which the curves of fig. 17 have been plotted.

As for other cases, sufficient curves are given to allow cross plotting, and fig. 18 shows a curve of maximum bending moment against K_1 for $\epsilon=60°$, which was obtained in this way.

Application of results to a wheel with a finite number of spokes.—The curves given in figs. 4, 5, 9, 12, and 17 may be used to determine sufficiently accurately the maximum values of the tensions, compressions, and bending moments in wheels having a finite but large number of spokes, as shown in the paper previously quoted. Suppose such a wheel has 2N spokes, the angular distance between two

TABLE V.

Values of maximum M/PR for Tangential Load.

K_1.	ϵ degrees.							
	0.	10.	30.	45.	60.	75.	85.	90.
0	−0·06417	−0·06417	−0·06417	−0·06417	−0·06417	−0·06417	−0·06417	—
10	−0·03748	−0·03756	−0·03860	−0·03926	−0·03960	−0·03656	−0·02644	0
50	−0·01973	−0·01983	−0·02046	−0·02128	−0·02196	−0·02082	−0·01577	0
100	−0·01441	−0·01457	−0·01510	−0·01586	−0·01663	−0·01620	−0·01267	0
200	−0·01055	−0·01060	−0·01106	−0·01169	−0·01252	−0·01256	−0·01000	0
600	−0·00630	−0·00636	−0·00664	−0·00711	−0·00777	−0·00821	−0·00689	0
1000	−0·00489	−0·00495	−0·00521	−0·00560	−0·00621	−0·00670	−0·00578	0

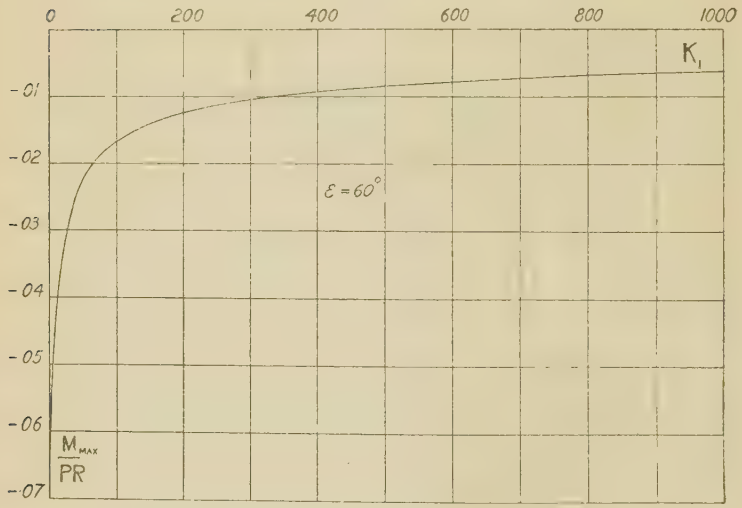
adjacent spoke attachment points in either system of spokes being 2θ (fig. 1) and let a_0 be the cross-sectional area of each spoke.

Then $$\Delta = \frac{Na_0}{2\pi R},$$

and $$K_1 = \frac{a_0 E_2 R^2}{E_1 I \theta}.$$

Maximum loads in spokes.—The curves of figs. 4, 5, and 12 gives values of Rt/P for the practical range of K_1, and

Fig. 18.



since t varies but little in the distance between adjacent spoke points it is sufficiently accurate in most cases to multiply the values taken from these curves by $2\theta P$ in order to find the maximum spoke loads. If more accurate estimates are required the appropriate curve of t can be plotted over a range $\pm\theta$ about the maximum value positions taken from figs. 6, 7, and 11, and the area integrated. Reference to the complete curves of t shown in figs. 3 and 10 indicate, however, that such refinement is usually unnecessary.

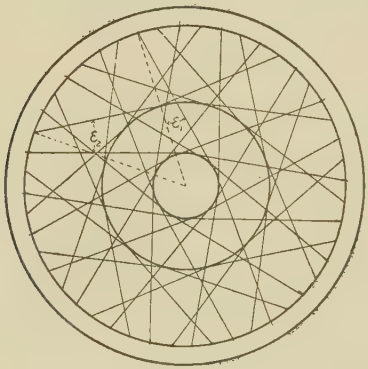
Maximum bending moment in the rim.—In the previous paper it was shown that when N was 30 or more the maximum bending moment in the rim was given very closely by

assuming that the number of spokes was infinite. Hence the curves in figs. 9 and 17 may be used directly to obtain the maximum bending moment.

Wheel with a quadruple spoke system.—The foregoing analysis deals with a wheel having a double spoke system, the spokes of these two systems being inclined at $\pm\epsilon$ respectively to the radii. In many wheels, however, the system is quadruple, the two additional sets of spokes being inclined at a different angle to those of the others; such an arrangement is shown in fig. 19.

Suppose the spokes to be inclined at $\pm\epsilon_1$ and $\pm\epsilon_2$ respectively, and let the tensions and compressions in the

Fig. 19.



disks of thickness Δ_1' and Δ_2' which replace these spokes in the analysis be t_1', t_2', t_1'', and t_2''. Then equations (7) become

$$\left.\begin{aligned} t_1' &= \frac{E_2\Delta_1'}{R}(u - v\tan\epsilon_1), \\ t_2' &= \frac{E_2\Delta_1'}{R}(u + v\tan\epsilon_1), \\ t_1'' &= \frac{E_2\Delta_2'}{R}(u - v\tan\epsilon_2), \\ t_2'' &= \frac{E_2\Delta_2'}{R}(u + v\tan\epsilon_2), \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (23)$$

and the equation for u becomes

$$\frac{\partial^6 u}{\partial \psi^6} + 2\frac{\partial^4 u}{\partial \psi^4} + \frac{\partial^2 u}{\partial \psi^2}(1 + K_1' \cos \epsilon_1 + K_2' \cos \epsilon_2)$$
$$- u(K_1' \sin \epsilon_1 \tan \epsilon_1 + K_2' \sin \epsilon_2 \tan \epsilon_2) = 0,$$

where $$K_1' = \frac{2R^3 E_2 \Delta_1'}{E_1 I_1},$$

and $$K_2' = \frac{2R^3 E_2 \Delta_2'}{E_1 I_1}.$$

Let K_0, ϵ_0 be the values of K and ϵ respectively which must be given to a wheel with two systems of spokes, so that the rim of this equivalent wheel will distort in exactly the same manner as that with the quadruple system. Then K_0, ϵ_0 must satisfy the conditions

$$\left.\begin{aligned} K_0 \cos \epsilon_0 &= K_1' \cos \epsilon_1 + K_2' \cos \epsilon_2, \\ K_0 \sin \epsilon_0 \tan \epsilon_0 &= K_1' \sin \epsilon_1 \tan \epsilon_1 + K_2' \sin \epsilon_2 \tan \epsilon_2, \end{aligned}\right\}. \quad (24)$$

and these give

$$\left.\begin{aligned} K_0^2 &= (K_1' \cos \epsilon_1 + K_2' \cos \epsilon_2)(K_1' \sec \epsilon_1 + K_2' \sec \epsilon_2), \\ \tan^2 \epsilon_0 &= \frac{K_1' \sin \epsilon_1 \tan \epsilon_1 + K_2' \sin \epsilon_2 \tan \epsilon_2}{K_1' \cos \epsilon_1 + K_2' \cos \epsilon_2}. \end{aligned}\right\}. \quad 25)$$

Then the double system wheel (K_0, ϵ_0) will have the same bending moments in the rim as that with four systems of spokes and the curves of maximum bending moment can be used directly. The tensions and compressions are found from equations (23) after u and v have been evaluated for the equivalent wheel.

Wheel in which the spokes are not in the plane of the rim.— In most wheels the spokes do not lie in the plane of the rim but are splayed so that they are able to resist side forces on the rim. Since half the spokes are splayed outward and half inward, distortion of the rim out of its plane for the loadings considered in this paper is very small and can be neglected.

Let the angle between the plane of the rim and the conical surfaces containing the spokes be ϕ. Then equations (7) become

$$\left.\begin{aligned} t_1 &= \frac{E_2 \Delta \cos \phi (u - v \tan \epsilon)}{R(1 + \cos^2 \epsilon \tan^2 \phi)}, \\ t_2 &= \frac{E_2 \Delta \cos \phi (u + v \tan \epsilon)}{R(1 + \cos^2 \epsilon \tan^2 \phi)}, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (26)$$

where t_1 and t_2 are the component stresses in the plane of the rim.

The value of K_1 for the wheel is then

$$K_1 = \frac{2\Delta E_2 R^3 \cos\phi}{E_1 I(1+\cos^2\epsilon\tan^2\phi)}.$$

The values of t taken from the curves of this paper must then be multiplied by $\sec\phi$ to obtain true stresses.

The authors desire to thank the Aeronautical Research Committee for permission to publish this paper.

XXIII. *Investigation of Uranothorites from the Arendal district, Norway.* *By* Ellen Gleditsch, *D.Sc., Professor of Chemistry, and* Bergliot Qviller, *cand. real., University, Oslo* *.

IT is well known that age calculations of radio-active minerals have for some time past been based on the respective contents of uranium and its disintegration product, radium G, in the minerals. Radium G is an isotope of lead, differing from ordinary lead by having an atomic weight of 206, while that of lead is 207·2. According to the disintegration theory 238 grams of uranium will give 206 grams of radium G and the amount of radium G (in grams) produced per year by one gram of uranium is $\lambda_u \cdot \frac{206}{238}$, where λ_u is the disintegration constant of uranium I.

The approximate age of the mineral will be given by the proportion $\frac{\text{RaG}}{\text{U}}$ found by analysis, multiplied by the inverse of the value given above :

$$\text{approx. age} = \frac{\text{RaG}}{\text{U}} \cdot 1{\cdot}155 \cdot \frac{1}{\lambda_u}.$$

If the value of λ_u be taken as $1{\cdot}52 \cdot 10^{-10}$ year^{-1} we get :

$$\text{approx. age} = \frac{\text{RaG}}{\text{U}} \cdot 7600 \text{ million years.}$$

It is evident that age calculations based on the quantities of radioactive substances present in the mineral are possible only when a certain number of mineralogical conditions are

* Communicated by Prof. A. Holmes, D.Sc., A.R.C.S., F.G.S.

fulfilled. First, the mineral must be old enough for radioactive equilibrium to have been attained. Secondly, it must be unaltered, none of the products formed through radioactive changes having been leached out. Thirdly, the accumulated radium G must not be contaminated by the presence of other isotopes, such as those of common lead, and contamination will undoubtedly have taken place if common lead entered into the mineral on its formation. A long series of investigations have resulted in the conviction that although small quantities of lead will often be found in the minerals, the proportion of lead to radium G in an old mineral is so small, that it is not necessary to take it into account in the first approximate age calculations. An atomic weight determination of the lead isotopes found in uranium minerals will, moreover, permit us to ascertain whether radium G occurs alone or in association with common lead. Another uncertainty is introduced by the presence of a certain amount of actinium D, the end product of the actinium series, having an atomic weight which cannot at present be said to be known with certainty. However, the amount of actinium D is very small (3–4 per cent.) compared with the amount of radium G and can be left out of consideration.

It must be said that the age calculations of old uranium-bearing minerals, based in earlier days on the $\frac{\text{lead}}{\text{uranium}}$ proportions, and later on the proportion of $\frac{\text{radium G}}{\text{uranium}}$ (involving atomic weight determinations), have on the whole proved very satisfactory. It would seem quite reasonable to apply the same method to the thorium-bearing minerals and calculate their age from the proportion of thorium D to thorium. On radioactive evidence no objection can be raised ; but the practical results of such calculations have been inconsistent among themselves, and, as a whole, they have not agreed with the age calculations based on the proportions $\frac{\text{radium G}}{\text{uranium}}$. The difficulties have led to the appearance of a number of different hypotheses concerning the end products of the thorium series. But on further investigation each hypothesis in turn had to be abandoned. The disintegration of the thorium series seems to be quite regular, the transformations leading finally to a stable end product, thorium D, an isotope of lead, with an atomic weight of almost exactly 208. Mineralogical considerations of the thorium minerals may, however, give

indications of the reason for the difficulties. The thorium minerals are, as a rule, more altered than the uranium minerals. Lawson * first suggested that they are secondary products, and consequently younger than the primary uranium minerals found in the same localities. This, however, seems to involve certain geological improbabilities. A. Holmes †, recently, in making the objection, pointed out that the wide variability of the lead proportions could be explained only by a process which affects some specimens more than others, *e. g.*, by a partial leaching out of the minerals by ground waters, hydrothermal or meteoric; he suggested that the deficiency of thorium D is due to the latter having been removed more easily than the radium G. This, in fact, seemed to make some of the direct results of analyses of uranium- and thorium-bearing minerals more consistent. Although the explanation may at first seem unlikely, thorium D and radium G being isotopic elements, further consideration makes it seem not improbable. The atoms of radium G generated where uranium-atoms initially occurred, will be surrounded by acid groups of UO_3, while atoms of thorium D will be produced in a less acid milieu, surrounded by much less acid groups of ThO_2, or perhaps bound as silicates, which can be more easily removed by percolating waters than the very insoluble uranates.

The amount of thorium D produced in a year by the disintegration of thorium is $\lambda_{Th} \cdot \frac{208}{232}$. The age of a thorium-bearing mineral ought to be given by:

$$\text{approx. age} = \frac{\text{ThD}}{\text{Th}} \cdot \frac{1}{\lambda_{Th}} \cdot \frac{232}{208}.$$

Most thorium minerals also contain small amounts of uranium, and many of the primary uraninites contain thorium. The lead isotopes found by analysis will then include both radium G and thorium D. If k be the amount of uranium which produces as much lead isotope as one gram of thorium, the approximate age is given by the expression:

$$\text{approx. age} = \frac{\text{Lead isotopes}}{\text{U} + k.\text{Th}} \cdot 7600 \text{ years},$$

$$\text{where } k = \frac{\lambda_{Th}}{\lambda_u} \cdot \frac{\frac{208}{232}}{\frac{206}{238}} = \frac{\text{Th}}{\text{U}} \cdot 1{\cdot}36.$$

* *Wien. Ber.* cxxvi. p. 721 (1917).
† Phil. Mag. (7) i. p. 1055 (1926).

Throughout this publication the value of λ_{Th} has been taken as $5{\cdot}3.10^{-11}$ giving $k=0{\cdot}36$. For discussions on the value of these constants see : ' Bulletin of the National Research Council,' No. 51, 1929 and No. 80, 1931 ('The Age of the Earth').

We have for several years been engaged in work on the radioactive minerals occurring in the southern part of Norway, and it seemed to us of interest to collect data to see if our experience confirmed the theory of a partial leaching of the thorium-bearing minerals. During last year, while we were still at work, the excellent treatise on ' The Age of the Earth ' was published. A good deal of work similar to the work we have been doing is there reported and correlated. In drawing conclusions we shall frequently refer to the sections by Professor A. Holmes and Professor A. Kovarik in the above-mentioned book. The experiments will be described in full.

The experiments were carried out on a group of thorites and especially on those rich in uranium, known as uranothorites. Like all thorites, they are *silicates* of thorium with varying quantities of iron, uranium and rare earths, but while in ordinary thorites the uranium content varies from 0·4–2 per cent. the uranothorites carry from 7·5 per cent. to 15 per cent. of uranium. This fact permits of a more accurate examination of the content of uranium and its disintegration products than is possible in the ordinary thorites.

The four specimens of mineral examined are typical uranothorites from the *Arendal district*. This lies in part of the Pre-Cambrian *Bamle formation* which stretches from Langesundsfjord to the south-west. The uranothorites examined are from the central part of the Arendal district, Riscer and Tvedestrand being within 40 km. from Arendal.

The chemical analyses of the specimens are recorded below.

The radium content was determined by the radium-emanation liberated, either in a radium solution prepared from the mineral and permitted to accumulate for a known period, or from the mineral itself at the moment of its solution in an acid. For details we refer to E. Gleditsch : ' Études sur les mineraux radioact.' *Archiv. for Math. og Naturvidenskab.* B. xxxvi. Nr. 1.

For some of the specimens both methods were used as a means of checking and complete agreement was achieved.

In Table II. some of the radioactive data for the minerals are given.

TABLE I.

Uranothorites from the Arendal district.

	1.	2.	3.	4.
	Tvedestrand.	Tvedestrand.	Krageroe.	Risoer.
SiO_2	29·30	18·53	18·41	15·78
Insoluble	9·48	3·41	3·23	1·09
Fe_2O_3	5·13	1·39	2·46	13·71
Al_2O_3	0·42	0·18	0·09	0·36
MnO	0·03	0·05	0·61	0·04
P_2O_5	0·24	0·19	0·39	0·36
CaO	1 98	1·79	2·10	1·05
MgO	0·57	0·21	0·18	0·19
PbO	1·31	1·70	1·03	0·69
U_3O_8	10·60	16·46	9·80	8·73
ThO_2	31·80	45·90	48·30	43·61
Rare earths (oxides)	1·90	1·66	1·46	3·30
H_2O	1·18	1·02	2·31	2·06
Loss of weight by calcination	6·22	7·14	9·72	9·25
	100·16	99·63	100·09	100·22
Specific density	3·65	4·44	3·94	4·14

TABLE II.

Mineral.	U %.	Th %.	Pb %.	Ra %	$\frac{Pb}{U}$.	$\frac{Ra}{U}$.	$\frac{Pb}{U+0{\cdot}36\,Th}$.	$\frac{Pb}{Ra}$.
ranothorite 1. Tvedestrand	8·99	27·95	1·22	$2{\cdot}83.10^{-6}$	0·136	$3{\cdot}20.10^{-7}$	0·064	0·43.10
„ 2. „	13·96	40·34	1·58	3·99 „	0·113	3·01 „	0·055	0·40 „
„ 3. Krageroe	8·31	42·45	0·96	2·29 „	0·116	2·76 „	0·041	0·42 „
„ 4. Risoer	7·41	38·33	0·64	1·47 „	0·086	1·98 „	0·030	0·44 „

First we notice that the $\frac{Ra}{U}$ value is lower in all the specimens than the equilibrium amount, $3{\cdot}40.10^{-7}$; it diminishes from $3{\cdot}20.10^{-7}$ in (1) to only $1{\cdot}98.10^{7}$ in (4). Turning then to the $\frac{Pb}{U+0{\cdot}36\,Th}$ ratio, we notice the same

variability: the values decrease from specimen (1) to specimen (4), and, moreover, they vary in approximate sympathy with the $\frac{Ra}{U}$ values. This proves that a possible leaching-out of lead is accompanied by a disappearance of radium also. There is an indication, however, that more thorium D has disappeared than radium G, for the proportion $\frac{Pb}{Ra}$ gives more nearly constant values than the $\frac{Pb}{U+0{\cdot}36\ Th}$ ratio.

The question also arises as to whether the radium has disappeared as such, or if an earlier member of the series has been removed, thereby occasioning a shortage in radium. It is evident that the epoch of the disappearance of radium will also be of importance, the disintegration into radium G being affected by any change in the earlier members of the series.

These very interesting points could be investigated more closely, and two ways suggested themselves to us: (i.) atomic weight determinations of the lead isotopes contained in the minerals; (ii.) evaluation of the ionium content of the minerals by a determination of the disintegration constant of radium. Unhappily the uranothorites are rare minerals, occurring only in small quantities. Of the specimens we had obtained, only one, No. 3, was large enough to permit of investigations along the two above-mentioned lines.

650 grams of the mineral was attacked in lots of 50 to 100 grams by hydrochloric acid, silica and insoluble residue being removed in the usual way. The filtered solutions were saturated with hydrogen sulphide and the sulphides removed for the atomic weight determination (1). The solutions were boiled in order to expel the excess of hydrogen sulphide; a small addition of nitric acid and boiling secured the oxidation of the metals present. The rare earths were then precipitated. In the first of the solutions (corresponding to about 100 gr. mineral) the rare earths were removed as fluorides. We should have preferred to use this method, which is undoubtedly the best, but the heavy bulk of rare earths and the necessity of handling the fluorides in platinum dishes made the operations too slow and difficult. We therefore precipitated the rare earths in the other solutions as oxalates which were filtered off; both fluorides and oxalates were transformed into sulphates (2). In the remaining mineral solution a small quantity of ionium-free rare earths was added; the rare earths were precipitated as fluorides, transformed to sulphates, and kept for a test solution (3).

(1) The sulphides were dissolved in nitric acid and transformed to sulphates by evaporation on a water bath with pure sulphuric acid. When only very little liquid was left, 50 per cent. alcohol was added and the sulphates filtered off. They were dissolved in ammonium acetate and again precipitated by hydrogen sulphide. The sulphides were dissolved in nitric acid and the nitrates were purified by repeated precipitations by concentrated nitric acid and recrystallizations from pure water in quartz and platinum.

A specimen of *pro analysé* lead-nitrate from Kahlbaum was chosen as "common lead" for comparison. It was purified in exactly the same manner as the lead from uranothorite.

The nitrates served for atomic weight determinations according to the method used first by Fajans and Lembert and later by one of us*. It consisted in comparing the specific density of saturated solutions of ordinary lead nitrate and lead nitrate prepared from the uranothorite. A series of careful experiments gave for the atomic weight of the lead isotopes from uranothorite a mean value of 207·00, ordinary lead being taken as 207·20. We did not, however, feel quite satisfied with the method, the errors on the separate weighings being too large, mainly, perhaps, owing to the fact that the material at hand, the nitrate from uranothorite, was so scarce (we had to use smaller pycnometers than we had planned), but partly owing to the difficulty of preparing a nitrate which includes neither nitric acid or basic nitrates. We therefore decided on a change of method and undertook a determination of the atomic weight of the lead isotopes by Richards's method based on silver and chlorine. The nitrates were transformed to chlorides, which again were recrystallized three times in quartz and platinum. Weighed amounts of the purified chloride were submitted to a distillation in quartz-tubes in a current of dry hydrochloric acid with subsequent cooling in dry nitrogen. After displacement of the nitrogen by dry air the chloride was reweighed and dissolved in hot water. Then followed precipitation by purest silver, and the end point was determined nephelometrically in the usual way.

Further details of this investigation will be given elsewhere †.

* *J. Chimie phys.* t. 22 (1925).

† This part of the work was done by Mrs. Falck Ytter and a more detailed account of it will be published later. We should like here to express our sincere thanks to Mrs. Falck Ytter for her most valuable help.

The values found were	207·026
and	207·006
Mean value	207·016

Purification of reagents followed the usual lines. Weighings were made by substitutions, a counterpoise being employed, and vacuum corrections applied.

If we assume—in a first approximation—that no common lead is present in the lead isotopes isolated from uranothorite 3 it is possible to evaluate from the atomic weight the amounts of the radium G and thorium D.

We have in fact:

$$208\ \text{Th D} + 206\ (100 - \text{Th D}) = 207{\cdot}02.100$$

and solving this we find:

Thorium D = 51 per cent.

Radium G = 49 per cent.

of the mixed isotopes, which again, of the 0·96 per cent. of lead isotope in the mineral, gives 0·47 per cent. radium G and 0·49 per cent. thorium D in the mineral. Accepting these values we now evaluate the proportions:

$$\frac{\text{Radium G}}{\text{Uranium}} = 0{\cdot}05656 \qquad \frac{\text{Thorium D}}{0{\cdot}36\ \text{Thorium}} = 0{\cdot}03206.$$

In an unaltered mineral where the radioactive changes have been going on undisturbed these two proportions should give the same value. The discrepancy, as will be seen, is much too large to be explained by the presence of lead or by experimental error and gives clear evidence that more thorium D than radium G has disappeared. The same fact is also borne out if we use the two proportions for age calculations:

$$\text{I.}\quad \frac{\text{RaG}}{\text{U}} \cdot 7600.10^{-6}\ \text{years} = 429{\cdot}9\ \text{million years.}$$

$$\text{II.}\quad \frac{\text{Th D}}{0{\cdot}36\ \text{Th}} \cdot 7600.10^{-6}\ \text{years} = 243{\cdot}6\ \text{million years.}$$

An age calculation based simply on the lead proportion would give:

$$\frac{\text{Pb}}{\text{U} + 0{\cdot}36\ \text{Th}} \cdot 7600.10^{-6} = 311{\cdot}6\ \text{million years.}$$

(2) The sulphates of the rare earths were dissolved in water. From the solutions the earths were repeatedly

precipitated by ammonia and redissolved in hydrochloric acid, which process should remove any radium present. After five precipitations the hydrates were dissolved, and the solutions transferred to two bulbs which were sealed up. From time to time their accumulated emanation was expelled by boiling and transferred to an electroscope where their ionizing power was measured.

(3) The solution was submitted to a treatment similar to that described above. In this case also the solution of purified hydrates was sealed up in a bulb and the production of radium emanation measured from time to time. The fact that this solution showed no increase in radium emanation proved that all the ionium in the mineral had been removed in the main precipitate, a necessary condition for getting a correct value of λ_{Ra}.

The radium production found by a series of analyses was $7{\cdot}446 \cdot 10^{-9}$ gram per year. The mineral contains $2{\cdot}29 \cdot 10^{-6}$ gram radium in 100 grams, consequently $1{\cdot}4885 \cdot 10^{-5}$ gram radium in 650 grams.

$$\lambda_{Ra} = \frac{7{\cdot}446 \cdot 10^{-9}}{1{\cdot}4885 \cdot 10^{-5}} = 5{\cdot}002 \cdot 10^{-4} \text{ year}^{-1},$$

corresponding to a half value period, T, of 1386 years.

By the same method earlier experiments on old and unaltered minerals have given the values $\lambda_{Ra} = 4{\cdot}11 \cdot 10^{-4}$ and $T_{Ra} = 1686$, values also accepted by the National Research Council of the National Academy of Sciences *.

It is evident from this result that the production of radium is too big in comparison with the amount of radium now present in the mineral. This fact was to be expected, the Ra/U ratio having been found much too low. It seems interesting to divide the rate of production of radium not by the amount of radium *now* found in the mineral, but by the amount of radium corresponding to the uranium in the mineral. The mineral contains 8·31 per cent. of uranium, which in 650 grams means 54·015 gram uranium. The equilibrium amount of radium corresponding to this should be $1{\cdot}8365 \cdot 10^{-5}$ gram, giving

$$\lambda_{Ra} = \frac{7{\cdot}446 \cdot 10^{-9}}{1{\cdot}831 \cdot 10^{-5}} = 4{\cdot}054 \cdot 10^{-4} \text{ and } T_{Ra} = 1709 \text{ years}.$$

This brings the λ_{Ra} value within reasonable limits.

* Bulletin of the National Research Council, No. 51, p. 14 (1929).

We could not expect very accurate results for this constant. In fact, the ionium-bearing hydrates, precipitated by ammonia, are voluminous and very difficult to wash out, so that some radium is likely to remain included. This makes the measurements of the small amounts of accumulating radium less precise.

The result does not give indication of any lack of ionium in the mineral. The leaching seems to have affected the radium and the lead, especially the thorium-lead.

Conclusions.

Chemical analyses have been made of a group of four uranothorites from the Arendal district in Norway. The radium-content has also been determined and other attempts made to find the relative amounts of the radioactive substances present in the minerals. The results prove that the minerals have been subject to alterations; the radium-uranium ratio is in all the specimens lower than the equilibrium value; the ratio $\frac{\text{Pb}}{\text{U} + 0{\cdot}36\ \text{Th}}$ varies from 0·06 to 0·03, which is lower than the average value for minerals from this district (see Table XXX. p. 288, in 'The Age of the Earth') and indicates a loss of lead. The loss of weight by calcination, the rather large amount of water, both evident from the analyses, and the low specific gravity corroborate the idea of an alteration in the composition of the minerals.

The lead isolated from a large amount of one of the uranothorites (No. 3) has served for an atomic weight determination and a subsequent calculation of the amounts of radium G and thorium D present. The ratio $\frac{\text{radium G}}{\text{uranium}}$ is found equal to 0·0556, while the ratio $\frac{\text{thorium D}}{0{\cdot}36\ \text{thorium}}$ is only 0·03206, which means that, admitting the usual radioactive disintegration, the mineral shows a deficiency of thorium lead.

The age of uranothorite 3 has been calculated:

(I.) on the $\frac{\text{radium G}}{\text{uranium}}$ ratio, giving 430 million years and

(II.) on the $\frac{\text{thorium D}}{0{\cdot}36\ \text{thorium}}$ ratio, giving 244 million years.

These are both much lower than the generally accepted value for the age of the minerals from the same area, viz., about one thousand million years. It therefore appears that lead

has been lost from uranothorite 3 and doubtless from the other uranothorites as well. And it seems further evident that thorium lead has been lost in greater proportion than uranium lead.

These different facts are most easily explained by accepting Professor Holmes's suggestion that the thorium minerals have been subject to a leaching-out by ground-waters and that this leaching has more particularly affected the thorium-lead.

The present investigation may be said to corroborate the theory put forward by Professor Holmes in his article Phil. Mag. (7) i. pp. 1055–1074 (1926).

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XXIV. *Gravitation and Electricity.* *By* Dr. Irene E. Viney, *Ph.D.*, *and* Prof. G. H. Livens, *M.A.* *

Introduction.

In 1923 Eddington † first propounded the idea that the gravitational and electromagnetic fields are the symmetrical and antisymmetrical parts of a more general tensor field. His affine geometry contains a fundamental tensor $G_{\mu\nu}$ which breaks up into symmetrical and antisymmetrical parts $R_{\mu\nu}$—or $g_{\mu\nu}$ with a suitable choice of gauge—and $F_{\mu\nu}$; the symmetrical tensor components are identified with the gravitational *potentials* and the antisymmetrical tensor components with the electromagnetic *forces*. More recently Einstein ‡, in formulating his general unitary field theory, which includes both electricity and gravitation as different aspects of a more general type of space-geometry, also evolves a similar idea, more especially however in considering an approximate form of a set of equations involving sixteen geometrical entities $h_{\mu\nu}$ §. He shows that in a field which

* Communicated by the Authors.

† *Cf.* his book 'The Mathematical Theory of Relativity,' pp. 198–212.

‡ *Sitzungsber. preuss. Akad. Wiss., Physik.-math. Kl.* cii. pp. 685–697 (1930).

§ In the general case these are not the components of a generalized tensor.

approximates very closely to a Euclidean field these quantities separate into a symmetric and an antisymmetric tensor, the one set satisfying equations of gravitational type and the other equations of electromagnetic type, both, however, in the very special case of free space devoid of matter or electricity. Similar ideas are cropping up more and more frequently in papers on this subject *, but always, however, in connexion with the geometrical ideas with which they were originally associated. It has not apparently occurred to any of the writers that the close association thus suggested between the two theories really implies the possibility of a formulation of a field theory for gravitational phenomena on similar lines to that employed so successfully in electromagnetic theory; and that, in fact, in so far as the complex ideas of curved space were unnecessary in the development of electromagnetic theory, so they should be equally unnecessary in developing a field theory for gravity. After all, if we are to have a unitary theory, it ought to be really unitary.

Recently, whilst examining certain attempts at generalizations of the classical electromagnetic theory, as expressed in Maxwell's equations and the associated dynamical theory, we discovered a generalized field theory † of the type suggested by Eddington and Einstein, in which the electromagnetic field separates out as the antisymmetric part and another field as the symmetric part, of a general second order tensor field, of a physical type however, so that it could in consequence be referred to any kind of space, Euclidean for preference. It then became a matter of interest to examine the possibility of developing the second and symmetric field as a field theory of gravity: and we were soon able to see that, by modifying a few of the conventional ideas about matter and the gravitational field in a way which proves ultimately to have little effect on the ultimate results, we could obtain an explanation of the main characteristics of gravitational phenomena in a real unitary theory.

We have not yet fully developed this new theory into all its numerous ramifications, but the success of our preliminary investigations seems sufficient to justify the publication of this preliminary account of the fundamental

* *Cf.* Einstein's renewed attempt at a unified theory, *Sitzungsber. preuss. Akad. Wiss., Physik.-math. Kl.* H. xxv. pp. 541–557 (1931); also C. Lanczos, *Zeitschr. f. Physik.* lxxiii. pp. 147–168 (1931).

† The first form of this theory was obtained by one of us (Dr. Viney) and incorporated in a thesis which was awarded the degree of Ph.D. in the University of Wales last June.

basis for the theory and of the few results which we have so far derived from it.

As the theory forms a simple counterpart of the electromagnetic theory it can be formulated without any of the elaborate invariantive analysis from which it was originally derived. At the outset, however, it will be of some convenience, and the connexion of our equations with the corresponding ones in electromagnetic theory will be immediately obvious, if we use the symmetrical four-dimensional form of the latter equations, taking x_1, x_2, x_3, x_4 for the three rectangular space-variables (x, y, z) and the imaginary time variable ict ($i=\sqrt{-1}$), c being the velocity of radiation.

General Formulation of the Theory.

As in electric theory the fundamental concept is that of a specific entity which, for want of a better name, we shall call *gravity* *, and which is associated with every particle of matter and enables it to act on every other similarly burdened particle in a manner to be subsequently specified, but which in the case of completely statical conditions is given by Newton's law

$$F = -\gamma g g'/r^2,$$

g, g' being the measures of the quantities of gravity associated with the particles, r their distance apart, and γ a constant depending on the units employed. The quantity g associated with a particle is not at present to be confused with the inertial mass of the particle (although this mass for a body comprising a whole series of such particles will be proportional to the total quantity of gravity contained in it). As electricity it is to be regarded rather as a separate entity associated with matter in more or less variable quantities; whether it can be separated from the matter (and what would be left if it were) and what relation it bears to the concept of electricity are questions for the future, but at least we can say that the form of the theory implies that it can occur with one sign only, and that the discovery of the non-electric particle (*Neutron*) as a constituent of matter at least lends colour to the suggestion that it may occur as a separate and separable entity.

As in electromagnetism we have, too, more or less continuous distributions of gravity determined by its volume

* Another word that suggests itself is *baricity*, and then the elementary particle would be called a *baron* or bariton (*e*).

density, μ, and also when the bodies carrying charges of gravity are in motion—with vector velocity $\mathbf{v}$—we shall have gravity currents determined by the vector volume density $\mu\mathbf{v}$.

Surrounding any system of masses there is a *gravitational* field which is in general defined in terms of ten *force* intensity components *, three being the usual statical components which the older theory recognized, one arising as a statical forcive due to the motions of the masses giving rise to the field, and the remainder becoming effective only under more general conditions of motion, much as the magnetic intensity acts on an electric particle only when it is moving. Adopting first the symmetrical form of the equations we shall use G_{rs} ($r, s = 1, 2, 3, 4$) to denote these force components: these are ten in number if we impose the restriction of symmetry $G_{rs} = G_{sr}$. Following now the lead of the electromagnetic theory, we introduce the four-dimensional current vector s defined by

$$s_r = \frac{\mu v_r}{c} \qquad r = 1, 2, 3,$$

$$s_4 = i\mu,$$

and then our first fundamental assumption is that the force components G_{rs} for any field are defined in terms of this vector by the equations

$$\frac{\partial G_{rs}}{\partial x_s} = -s_r,$$

where we employ the usual summation convention for repeated indices. These equations correspond to the set expressing Ampère's Law in electromagnetism, but whereas the latter set are expressed in terms of an antisymmetric tensor, with the possibility of a change of sign, our present equations do not admit of any such possibility; this is possibly the gist of the reason for the occurrence of two types of electricity but only one type of gravity.

* The ten *potentials* of the relativity discussions. It is interesting to see how all writers seem almost hypnotized by the word potential as used in this connexion. After resolving a general second order tensor into its symmetric and antisymmetric parts, they calmly identify the components of one part with *potentials* and the components of the other part with *forces*, without realizing that no real physical tensor can be of such a hybrid nature. And this indifferent mixing up of physical terms —justified only in purely geometrical theory where all physical characteristics but magnitude and direction are discarded—has not been without its influence on the general development of the theory itself; simple potential solutions of the equations always being sought when force solutions are equally applicable and probably more appropriate.

The set of equations corresponding to the usual expression of Faraday's Law does not form a part of this theory, but the equivalent set of equations expressing the electric and magnetic force intensities in terms of four potentials * have their counterpart in the symmetric equations

$$G_{rs} = -\frac{\partial \phi_r}{\partial x_s} - \frac{\partial \phi_s}{\partial x_r} \dagger.$$

From these last equations we obtain, by differentiation,

$$-s_r = \frac{\partial G_{rs}}{\partial x_s} = -\frac{\partial^2 \phi_r}{\partial x_s \partial x_s} - \frac{\partial}{\partial x_r}\left(\frac{\partial \phi_s}{\partial x_s}\right),$$

and, if we take over the usual relation of electric theory which defines the simple retarded potentials, viz.,

$$\frac{\partial \phi_s}{\partial x_s} = 0,$$

we derive also the fundamental potential equation

$$\frac{\partial^2 \phi_r}{\partial x_s \partial x_s} = s_r,$$

so that, in a way, the ϕ's are the retarded potentials of the gravitational field. The standard solutions are of the usual type, so that

$$\phi_r = -\frac{1}{4\pi}\int [s_r]\frac{dv}{r},$$

the square bracket notation denoting as usual the values of the functions included at the time $t - r/c$.

This shows at once that in a purely statical field our theory reduces to the familiar one for the ordinary Newtonian field; for in that case $\phi_1 = \phi_2 = \phi_3 = 0$, and

$$\phi_4 = i\phi = -\frac{i}{4\pi}\int \mu \frac{dv}{r},$$

* $$F_{rs} = -\frac{\partial \phi_r}{\partial x_s} + \frac{\partial \phi_s}{\partial x_r},$$

ϕ_1. ϕ_2, ϕ_3 being the components of the usual vector potential and $\phi_4 = ic\phi$, where ϕ is the usual scalar potential of the field.

† C. Lanczos, in his paper mentioned at the beginning, obtains a similar expression for G_{rs}, but his potentials are the same as those involved in the definition of F_{rs}—that is they are precisely the electromagnetic potentials. This is of course absurd, as it implies such an interrelation between the two fields that one cannot exist without the other. In our theory the use of different conditional equations for the G's enables us to introduce entirely different ϕ's to those involved with any electromagnetic field, and there is no implication of any interaction at all.

and ϕ is the usual Newtonian potential. In this case

$$G_{14}=-i\frac{\partial\phi}{\partial x_1},\ G_{24}=-i\frac{\partial\phi}{\partial x_2},\ G_{34}=-i\frac{\partial\phi}{\partial x_3}$$

reduce to the usual force intensity components, and all the other G's are zero.

This formally completes the kinematical specification of the field. This is, however, useless without some dynamical relation determining the force on a moving element, or at least something equivalent to this determination. Here, however, we have to depart from our close analogy with the electromagnetic case. In fact, if the analogous form for the Lagrangian function of the field is assumed, viz.,

$$-\iiint G_{rs}\,dx_1dx_2dx_3{}^*,$$

as is actually suggested by Eddington, who, however, does not pursue the argument further, then the general analysis by least action shows that the force per unit volume on the masses in the field is given by its three components

$$F=-s_sF_{sr}\qquad r=1,\ 2,\ 3,$$

that is, by the corresponding components of the field intensity, as if it were of electromagnetic origin, instead of by the expression

$$F_s=-s_sG_{rs},$$

as is suggested by a rigid pursuit of the analogy between the two theories. As, however, this latter form leads to very serious difficulties of another kind, it seems better to retain the form suggested for the action integral, and all the consequences which follow from it, even if they do not quite fit the picture one was inclined to expect.

The fourth component of the force is, of course, interpreted as usual in terms of the activity of the force.

The fact that the force on the moving masses and its activity expressed in terms of a different tensor to that which defines the field of the particles is perhaps a little disconcerting; but in the way in which we have framed the theory this result seems inevitable, in spite of the fact that it deprives the field tensor G_{rs} of a good deal of its physical significance and transfers it to the accompanying tensor F_{rs}. Our choice of potentials is, however, such as to make the difference between

* The negative sign is to be noticed. It is required to obtain the correct sign to the force on a charge, and is of fundamental importance in the development of the theory.

the two tensors almost negligible, so possibly no serious harm can arise ; but this is a point which is being reserved for attention.

It is now quite easy to reduce these results to the simple real time and ordinary (x, y, z) coordinates. We see that, using the electrical notation of **A** for a vector potential and ϕ for a scalar potential,

$$\mathbf{A} = -\frac{1}{4\pi c}\int [\mu \mathbf{v}]\frac{dV}{r},$$

$$\phi = -\frac{1}{4\pi}\int [\mu]\frac{dV}{r},$$

and both **A** and ϕ satisfy equations of the form

$$\frac{\partial^2\chi}{\partial x^2}+\frac{\partial^2\chi}{\partial y^2}+\frac{\partial^2\chi}{\partial z^2}-\frac{1}{c^2}\frac{\partial^2\chi}{\partial t^2}=\mathrm{K},$$

and also the relation

$$\mathrm{div}\ \mathbf{A}+\frac{1}{c}\frac{\partial\phi}{\partial t}=0.$$

Of the ten G's the following seven are real :

$$\mathrm{G}_{11}=-2\frac{\partial \mathrm{A}_x}{\partial x},\qquad \mathrm{G}_{22}=-2\frac{\partial \mathrm{A}_y}{\partial y},\qquad \mathrm{G}_{33}=-2\frac{\partial \mathrm{A}_z}{\partial z},$$

$$\mathrm{G}_{12}=-\left(\frac{\partial \mathrm{A}_x}{\partial y}+\frac{\partial \mathrm{A}_y}{\partial x}\right),\qquad \mathrm{G}_{23}=-\left(\frac{\partial \mathrm{A}_y}{\partial z}+\frac{\partial \mathrm{A}_z}{\partial y}\right),$$

$$\mathrm{G}_{31}=-\left(\frac{\partial \mathrm{A}_z}{\partial y}+\frac{\partial \mathrm{A}_y}{\partial x}\right),\qquad \mathrm{G}_{44}=-\frac{2}{c}\frac{\partial\phi}{\partial t}.$$

The remaining three are imaginary ; if we introduce another notation for their real forms, calling them X, Y, Z, we have

$$\mathrm{X}=-\frac{\partial\phi}{\partial x}+\frac{1}{c}\frac{\partial \mathrm{A}_x}{\partial t},\qquad \mathrm{Y}=-\frac{\partial\phi}{\partial y}+\frac{1}{c}\frac{\partial \mathrm{A}_y}{\partial t},$$

$$\mathrm{Z}=-\frac{\partial\phi}{\partial z}+\frac{1}{c}\frac{\partial \mathrm{A}_z}{\partial t}.$$

The equations connecting these force intensities with the gravity and current densities are of the type

$$\frac{\partial \mathrm{G}_{11}}{\partial x}+\frac{\partial \mathrm{G}_{12}}{\partial y}+\frac{\partial \mathrm{G}_{13}}{\partial z}=-\frac{\mu \mathrm{v}_x}{c}-\frac{1}{c}\frac{\partial \mathrm{X}}{\partial t},$$

whilst

$$\frac{\partial \mathrm{X}}{\partial x}+\frac{\partial \mathrm{Y}}{\partial y}+\frac{\partial \mathrm{Z}}{\partial z}=-\mu-\frac{1}{c}\frac{\partial \mathrm{G}_{44}}{\partial t}.$$

The tensor F_{rs} has, as in electromagnetic theory, three real components (F_{12}, F_{23}, F_{31}) and three imaginary components (F_{14}, F_{24}, F_{34}) which are expressed in terms of **A** and ϕ by the usual equations of electromagnetic type,

$$F_{23}=\frac{\partial A_z}{\partial y}-\frac{\partial A_y}{\partial z}=H_x,$$

and

$$F_{14}=-\frac{i}{c}\frac{\partial A}{\partial t}-i\frac{\partial \phi}{\partial x}.=iEx\ ;$$

and finally the force on a moving charge is determined by the vector

$$E+\frac{1}{c}[vH],$$

expressing the force per unit charge.

This concludes the formal specification of the theory in its most general form. It now remains to examine certain definite applications to particular problems to see to what extent the results derived from it are in agreement with the observed facts. Before we leave this general exposition we may make two remarks which will save us going in the next section into any detail about our calculations. The first of these is that our original method of deriving the theory by an invariantive or least action method ensures that our specification satisfies all the necessary criteria of both the restricted and general theory of relativity—that is, that our equations can all be formulated in such a way that they remain completely invariant under any possible transformation of axes, and in particular for the Lorentz transformation of the restricted theory of relativity. This remark is important, as it establishes the validity of such phenomenon as the variation of inertia mass with velocity and the contraction of a moving mass in the direction of its motion—the Fitzgerald-Lorenz contraction.

The second remark is that it is obvious from the form of our equations that the analytical development of our theory follows very closely along the familiar and well-worn lines of electromagnetic theory; it will not therefore be necessary for us to enter into any elaborate explanation of any results carried over from that theory. In so far as there may be any difference the calculations will be given in full on another occasion.

Discussion.

Before the theory is developed in any detail there are certain points in connexion with its formal justification on

physical grounds which call for immediate attention and exposure.

In the first place it will be seen that—as in electromagnetism—the inertial mass of a moving body is proportional to the *square* of its gravitational mass. This result apparently contradicts the fundamental law of physics which asserts that these two masses are proportional to one another under all conditions. It must however be realized that this law is established only for a body of finite mass—containing as we know a large collection of more or less identical elements (for our purposes this element might be taken to be a combination of a proton and electron *)—and also we must remember that the two masses—inertial and gravitational—of such a body are both proportional to the number of these elements contained in it, and then it is not difficult to see that our assumption does not in reality contradict this law if only we can assume that the gravity charges are concentrated into small nuclei and not spread uniformly throughout even an atom †.

The possibly more interesting result that the gravitational inertial mass proves to be negative ‡ is also, in reality, no less disturbing. In fact the gravitational charge on any element of matter is almost incomparably small in comparison with the electrical charges known to be associated with any such element—the ratio is of the order 10^{-16},—so there is probably little chance of any peculiar phenomena manifesting themselves on this account. Such phenomena do, however, occasionally present themselves, and it may be that we have here at least a partial explanation for them, and in this connexion it is perhaps not irrelevant to remember that Dirac has found it convenient to regard the positive electrical element as an entity possessing negative kinetic energy. The actual inertia of an active particle (gravitational or electric) is not only a function of the charge but also of the degree of its concentration, and a charge, however small, may still have a preponderating inertia if sufficiently condensed.

The question of the interaction of electricity and gravity also seems well beyond the possibility of detection under

* Assuming, of course, that everything else, if there is anything else, in matter is divided up between these constituents in equal proportions.

† As a matter of fact, of course, Einstein's theory does not in reality involve any more specific assumption about the proportionality of inertial and gravitational masses: it really concerns itself simply and solely with gravitational mass, as, there being no forces to bring it into evidence, the inertial mass really finds no place in the theory.

‡ This arises from the negative sign which has to be taken with the least action function to secure consistency in other ways.

present laboratory conditions ; it is impossible to prevent an electric field from altering the electrical condition of any body placed in it, thus giving rise to electrical forces far greater than the forces exerted by the field on the gravity charges involved. The only possibility then that remains is the effect of an intense gravitational field on electrified bodies, such, for example, as the effect of the earth in attracting electrified particles to it ; here again, however, the effect is so small for any realizable charge that it is very doubtful whether the most refined experiment would detect it. Experiments have, however, been conducted to detect an effect of this kind, and without negative results, and we will therefore return to this question on another occasion.

The next question that naturally arises is as to the effect of the additional and quasi-magnetic or motional forces which act on matter according to our theory, and as to the reason that they have so far escaped detection. Here again it is also a case of relative magnitudes and the forces being masked by others of a much larger kind. It must be remembered that in the electromagnetic field the magnetic forces are generally very small (in the ratio $1 : c$) compared with the electric forces, and that it is only the possibility of the cancelling (positive and negative) of the electric forces that enables us to separate them out and examine their characteristics independently. In the gravitational case this cancelling process is impossible, there being only one sign of charge, and therefore the comparatively small motional forces are always masked by the much larger static ones. In view, however, of the great degree of accuracy obtained in astronomical measurement this general statement requires somewhat closer examination, and we have therefore worked out in some detail the simple problem of two electrically neutral particles with positive inertia but each with a charge of *gravity*, and moving under their mutual attraction. The result of this calculation—not unlike similar and familiar ones in electromagnetic theory—is that in a problem of this kind the modifications we have introduced into the law of interaction are completely ineffective in modifying the truth of the simple static inverse square law to the degree of accuracy attainable in the measurement of planetary phenomena. In spite, that is, of the entirely changed point of view, which requires that all gravitational effects are propagated with the velocity (c) of electromagnetic radiation *, and that bodies in motion have additional forces

* A finite velocity of propagation has long been known to be ineffective in modifying the effective law of gravitational action, and is also required by the relativity theories.

acting on them on account of their motion, our theory thus fully substantiates the accuracy of the inverse square law in so far as it applies to planetary phenomena in the solar system. It does, however, obviously offer possibilities for the explanation of more or less speculative discrepancies in phenomena of a different order of magnitude—stellar on the one side and atomic on the other—to those pertaining in the solar system. This is, however, merely a pious hope that further development of the theory may reveal its usefulness, at least, in elucidating some of the numerous difficulties which still present themselves in all such physical problems—in the large and in the small.

We have stated that the additional complications of our theory have no appreciable effect in planetary motion problems; this statement is, however, subject to one rather important reservation, as there is a small modification which has an appreciable effect in the case of the planet Mercury. Our theory leads, in fact, as does the electromagnetic theory, to the result that the inertial mass of a moving particle varies with its velocity, and the law of variation is the same in the two cases. If this is assumed, then it is easy to see that it leads to an advance in the perihelion of a planetary orbit by an amount which is just one sixth of that given by Einstein's formula. It is perhaps a little disappointing that the theory does not give a larger value, but it is to be remembered that all unitary theories constructed on the relativity basis suffer from the same defect. The only one which has been developed to any extent in this direction is that given by Einstein, and his result—he does not give it, for obvious reasons—is identical with ours. It is, of course, just possible that our theory has still to be supplemented by Einstein's original discussion—regarded as an attempt to discover a correct form for the Lagrangian function of a particle moving in a field of force,—but then the unification of the theories of gravitation and electricity is to be obtained, not on the lines of his later theories, but by introducing electricity into his first theory in the same way as he introduces matter, and not through the electromagnetic stress energy tensor. Such a modification seems to have not a few reasons in its favour and might be capable of experimental verification.

The only other question of a general nature which seems to present itself in the development of a field theory of the above character is the question of the influence of the character of an intervening medium on the gravitational force between two bodies. In other words, is there any sort of dielectric action by the intervening medium? When we

remember, however, that the dielectric action of matter arises solely from the polar constitution of its molecules, and as we are bound from the general nature of the case to restrict ourselves to one kind of *gravity* only—whether it is positive or negative in the electrical sense is entirely irrelevant,—it is at once obvious that nothing in the nature of dielectric action can manifest itself, and that therefore the only action of an intervening body will be to add its own undisturbed gravitational field to the general action between the bodies it separates. This at least is the result in a statical field. A difference in the gravity charges on the positive and negative electric constituents of matter might easily involve a very decided influence of a body on the propagation of gravitational waves through it, but this is a phenomenon that has not yet entered the realm of physics.

In conclusion, therefore, we can say that our theory seems to offer a reasonable solution to the problem of determining a field theory for gravitational phenomena. While it has not so far been developed to explain all the minute phenomena covered by Einstein's earlier theory, it does at least go as far as any of the later unitary theories, and has, in addition, the great advantage of being a physical theory which can be described therefore by reference to a Euclidean or, at will, any other type of space. What possibilities it offers in other directions must be settled by the future when time allows for its further development. It is obvious, however, that if substantiated the theory will open up numerous questions of fundamental importance to physical science, since the gravitational field can now assume at least part responsibility for a large number of phenomena presumed, at present, to arise solely from the electrical constitution of matter.

Cardiff.
April 8th, 1932.

XXV. *On the Propagation of Elastic Waves in Materials under High Hydrostatic Pressure.* *By* H. Hencky, *Mass. Inst. of Technology* *.

Introduction.

FROM physical and geological evidence we know that the density and the hydrostatic pressure in the interior of the earth increases with increasing depth. Geologists have

* Communicated by the Author.

estimated that the pressure in the centre of the earth amounts to about

$$p_c = 3{,}000{,}000 \text{ atm. or } 43{,}000{,}000 \text{ lb./sq. inch.}$$

This value is about twice that for the modulus of compression of iron. With a parabolic distribution of pressure along the earth-diameter this would mean that the greater part of the earth-interior is subjected to a hydrostatic pressure, the magnitude of which is of the same order as the moduli of elasticity of the material comprising the earth-interior.

It seems therefore worth while to examine the influence of an existing hydrostatic stress on the velocity of sound-waves. Such an examination is needed especially because of the far-reaching conclusions which are drawn from earthquake observations.

We will derive in this paper the corrections for the velocities of propagation. The velocity of the propagation of compression waves is especially influenced by the existing hydrostatic pressure.

The Equations for Small Movements.

We neglect the fact that the pressure is not a constant because the influence of the changes in pressure is of the same order of magnitude as the volumetric forces, which are also not very important.

Assuming a small displacement u, v, w, the equations of movement in a fixed rectangular system of coordinates take the following well-known form:

$$\left.\begin{aligned} \frac{\partial \sigma_x}{\partial x} + \frac{\partial \tau_z}{\partial y} + \frac{\partial \tau_y}{\partial z} &= \rho \frac{\partial^2 u}{\partial t^2} \\ \frac{\partial \tau_z}{\partial x} + \frac{\partial \sigma_y}{\partial y} + \frac{\partial \tau_x}{\partial z} &= \rho \frac{\partial^2 v}{\partial t^2} \\ \frac{\partial \tau_y}{\partial x} + \frac{\partial \tau_x}{\partial y} + \frac{\partial \sigma_z}{\partial z} &= \rho \frac{\partial^2 w}{\partial t^2} \end{aligned}\right\} \quad . \quad . \quad . \quad (1)$$

The stresses σ_x, σ_y, σ_z, τ_x, τ_y, τ_z are caused by the displacement u, v, w. The total stresses are $\sigma_x - p$, $\sigma_y - p$, $\sigma_z - p$, τ_x, τ_y, τ_z.

It is important to notice that these stresses are the true physical stresses at a certain moment t; they are not related to the surfaces in the state of rest $u = v = w = 0$.

The equations (1) connecting forces and accelerations must be completed by a proper law of elasticity, and here we meet a difficulty. Although this is often neglected, the

common law of Hooke is absolutely unfit to treat *finite* deformations.

However, it can be shown rigorously that the strain must be defined by the differential equation

$$\text{Differential of strain} = \frac{\text{infinitesimal increase in length}}{\text{instantaneous length}}.$$

The strain itself is then the hyperbolical logarithm of the ratio

$$\frac{\text{length after deformation}}{\text{length before deformation}}\ *.$$

Taking now the principal axes of strain as axes of reference, and denoting the strains with ϵ_1, ϵ_2, ϵ_3, the principal stresses with S_1, S_2, S_3, we state, as the law of elasticity,

$$\left.\begin{aligned} S_1 - S &= 2G.e^{-3\epsilon}(\epsilon_1 - \epsilon) \\ S_2 - S &= 2G.e^{-3\epsilon}(\epsilon_2 - \epsilon) \\ S_3 - S &= 2G.e^{-3\epsilon}(\epsilon_3 - \epsilon) \end{aligned}\right\} \quad . \ . \ . \quad (2a)$$

where

$$S = \tfrac{1}{3}.(S_1 + S_2 + S_3) \quad \text{and} \quad \epsilon = \tfrac{1}{3}(\epsilon_1 + \epsilon_2 + \epsilon_3)$$

and

$$S = K.e^{-3\epsilon}.3\epsilon. \quad . \ . \ . \ . \ . \quad (2b)$$

The difference between this law and the law commonly used in treatises of elasticity lies in the factor $e^{-3\epsilon}$ and in the logarithmic measure of the strains; however, for infinitely small strains the difference disappears.

For finite strains the experiments of Bridgman † show the necessity of such a factor as $e^{-3\epsilon}$. Theoretically, this factor is needed to make the existence of an elastic potential possible. The work done is, namely,

$$\delta W\, dx_1 dx_2 dx_3 = S_1 \overline{dx_2}\,\overline{dx_3}\,\delta\overline{dx_1} + S_2 \overline{dx_1}\,dx_3 . \delta\overline{dx_2} + S_3 \overline{dx_1}\,\overline{dx_2} . \delta\overline{dx_3},$$

the bars indicating the length after deformation.

With

$$e^{3\epsilon} = \frac{\overline{dx_1}\,\overline{dx_2}\,\overline{dx_3}}{dx_1 dx_2 dx_3},$$

we get

$$\delta W = e^{3\epsilon}.(S_1\delta\epsilon_1 + S_2\delta\epsilon_2 + S_3\delta\epsilon_3). \quad . \ . \ . \quad (3)$$

* Compare 'Journal of Rheology,' ii. no. 2, pp. 169–176 (1931).

† *Cf.* A. Nadai, 'Plasticity,' p. 13. McGraw Hill Book Co. (1931).

This expression can become a total differential only if the formula of the stresses contains a compensating factor $e^{-3\epsilon}$. Only in this case therefore does an adiabatic elastic potential exist.

Differentiating now (2*a*) and (2*b*) and considering that the initial stresses $S_i - S$ are 0 in our case and $S = -p$, we find

$$\begin{aligned}\delta(S_i - S) = \sigma_i - \sigma &= 2G.e^{-3\epsilon}.(\delta\epsilon_i - \delta\epsilon)\\ \delta S = \sigma \quad &= K.e^{-3\epsilon}.3.\delta\epsilon - 3K.e^{-3\epsilon}.\epsilon.3\delta\epsilon\\ &= K.e^{-3\epsilon}\ 3.\delta\epsilon - S.3.\delta\epsilon.\end{aligned}$$

Going over to an arbitrary orientation of the coordinate system we have to put in the place of $\delta\epsilon_1$, $\delta\epsilon_2$, $\delta\epsilon_3$ the six components of infinitesimal strain

$$\frac{\partial u}{\partial x}\ \frac{\partial v}{\partial y}\ \frac{\partial w}{\partial z},\quad \frac{1}{2}\left(\frac{\partial w}{\partial y}+\frac{\partial v}{\partial z}\right),\quad \frac{1}{2}\left(\frac{\partial u}{\partial z}+\frac{\partial w}{\partial x}\right),\quad \frac{1}{2}\left(\frac{\partial u}{\partial y}+\frac{\partial v}{\partial x}\right).$$

We get, finally,

$$\left.\begin{aligned}\sigma_x - \sigma &= 2G.e^{-3\epsilon}\left\{\frac{\partial u}{\partial x} - \frac{1}{3}\left(\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}+\frac{\partial u}{\partial z}\right)\right\}\\ \sigma &= (K.e^{-3\epsilon}+p)\left(\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}+\frac{\partial v}{\partial z}\right)\\ \tau_x &= 2Ge^{-3\epsilon}\frac{1}{2}\left(\frac{\partial w}{\partial y}+\frac{\partial v}{\partial z}\right)\end{aligned}\right\}. \quad (4)$$

Cyclical permutation gives the other equations.

Eliminating the average stress, σ gives

$$\sigma_x = 2G.e^{-3\epsilon}\frac{\partial u}{\partial x} + \left(K.e^{-3\epsilon} - \frac{2Ge^{-3\epsilon}}{3} + p\right)\left(\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}+\frac{\partial w}{\partial z}\right).$$

Equations (1) and (4) together yield three equations for the unknown displacements u, v, w. It will be convenient to write

$$\Delta = \frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}+\frac{\partial w}{\partial z}.$$

The result is

$$\left(K + \frac{1}{3}.G + p.e^{3\epsilon}\right)\frac{\partial \Delta}{\partial x} + G.\nabla^2 u = \rho.e^{3\epsilon}.\frac{\partial^2 u}{\partial t^2}, \quad (5)$$

with two analogous equations for v and w

$$\left(\nabla^2 = \frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right).$$

As $e^{3\epsilon}$ is the relative volume, the expression $\rho . e^{3\epsilon}$ means the density which the material would assume if the pressure p would be taken away.

Differentiating equations (5) with respect to x, y, z and adding, gives the equation for the compression and tension waves,

$$\left(\mathrm{K}+\frac{4}{3}.\mathrm{G}+p.e^{3\epsilon}\right).\nabla^2\Delta=\rho.\frac{\partial^2 u}{\partial t^2}. \quad . \quad . \quad (5a)$$

Analogously we get the three equations for the rotations

$$\omega_x=\frac{1}{2}\left(\frac{\partial w}{\partial y}-\frac{\partial v}{\partial z}\right),$$

$$\mathrm{G}.\nabla^2\omega_x=\rho_0.\frac{\partial^2\omega_x}{\partial t^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5b)$$

The values of $e^{3\epsilon}$ will always lie between $\frac{1}{2}$ and 1. The velocity of the compression waves becomes

$$v_c=\sqrt{\frac{\mathrm{K}+\frac{4}{3}\mathrm{G}+pe^{3\epsilon}}{\rho_0}}, \quad . \quad . \quad . \quad . \quad (6a)$$

and the velocity of the shear waves will be

$$v_s=\sqrt{\frac{\mathrm{G}}{\rho_0}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6b)$$

As ρ_0 decreases with increasing pressure we should expect an increase of the velocity of the waves in general with the depth. The compression waves have also in the numerator a correction due to p. Putting, for the sake of simplicity, $e^{3\epsilon}=1$, we would get a correction of the classical formula, containing only $\sqrt{\mathrm{K}+\frac{4}{3}.\mathrm{G}}$, of 40 per cent. for the special case $\mathrm{K}+\frac{4}{3}\mathrm{G}=p$.

It is evident that we could have solved in the same manner the inverse problem, namely, given the velocity of the waves to determine which law of compression holds good in the interior of the earth.

XXVI. *Investigations on Polarization of Light-Scattering.*—Part I. *By* S. Venkateswaran *.

Introduction.

THE discovery of the Raman effect, besides introducing to the scientific world several new types of combination scattering whose frequencies are different from that of

* Communicated by Sir C. V. Raman, M.A., D.Sc., F.R.S., &c.

the incident light, has also necessitated a complete revision of the existing theories regarding even the classical scattering of unaltered frequency. In the development of the theory of the Raman radiations, as also in the revision of the theories of classical scattering, an investigation of their polarization is of considerable help. In fact, the small depolarization of the light transversely scattered by the molecules in the gaseous state supplies a most accurate measure of the optical anisotropy of the molecules, a quantity which plays a very important part in the discussions on electric and magnetic double-refraction phenomena.

In the earlier theories due to Lord Rayleigh and Born no change of wave-length in scattering is contemplated, and the measurements on polarization have all been made with white incident light, either directly or filtered through coloured glasses. But our newer knowledge, derived from the discovery of the Raman effect, points to the necessity in these measurements of using monochromatic illumination and separating the radiation of unaltered frequency from the Raman radiations. An analysis of the polarization of these radiations as isolated from the Raman radiations, especially those arising from the combination of the frequency of the incident light with the small rotational frequencies of the molecules, is naturally of considerable interest, and was therefore undertaken by the present writer. The first part of the paper describes the results of such measurements and the unique manner in which they point to the unsatisfactory nature of the earlier quantum theories of scattering, and lends a strong support to the theory of the spinning photon, recently suggested by Prof. Raman and Bhagavantam *. The relation of such measurements to the older measurements on the aggregate scattered radiations is also discussed.

Again, apart from the Raman radiations disturbing by their admixture the polarization of the unmodified scattering, the polarization of the former by themselves is also of great theoretical value ; since the state of polarization of any given Raman frequency representing a particular type of oscillation is intimately connected with its dynamics, and hence any theory of the Raman scattering before it can be considered satisfactory has to explain the fundamental facts of polarization. For this reason a large number of typical liquids have been investigated and their Raman lines have been carefully measured for their polarization. A detailed report of these measurements is presented in Part II.

* Ind. Journ. Phys. vi. p. 353 (1931).

Relation to other Types of Scattering.

As is well known, when a beam of monochromatic radiation is sent through a transparent medium and the scattered light is analysed with the help of a spectroscope, it is found to contain, in addition to the classical scattering of the same frequency as the incident, also Raman radiations of different kinds, viz., vibrational Raman lines, arising from a combination of the incident frequency with the oscillation frequencies of the molecules, rotational Raman lines due to similar combination with the rotational frequencies of the molecules, and the vibration-rotation lines arising from a combination of both. In addition there is also a continuous spectrum whose intensity varies from substance to substance. Of these, the vibrational lines in most cases are comparatively very feeble, and their total intensity is only a small fraction of the intensity of the classically scattered line. Also, since these lines are more or less partially polarized in the same direction as the classically scattered line, their admixture with the latter is not likely to influence considerably the measurement of polarization of the classical scattering. On the other hand, the aggregate intensity of the rotational Raman lines is not small, and these lines are so close to the classical line and are so nearly unpolarized that their influence on the polarization of the classical line due to the admixture will be considerable, and the same thing is also true in some cases of the continuous spectrum. Hence it is of the utmost importance in measurements on the polarization of the classically scattered line, not only to use monochromatic light for excitation but also to analyse the scattered radiation, spectroscopically so as to separate the radiations for which the polarization is to be studied from the other radiations which always accompany them.

Experimental.

The general method of measurement is as follows :—

A portion from the middle of a mercury arc-lamp was isolated with the help of a small aperture in an opaque screen, and it was focussed at the centre of a spherical bulb containing the liquid. The transversely scattered light was analysed with the help of a high-dispersion glass spectrograph, the axis of whose collimator was adjusted to be exactly normal to the direction of the track. Since the principal components of the partially polarized scattered light entering the spectroscope are vertical and horizontal,

by placing in front of the slit of the spectroscope a nicol with its vibration axis vertical and horizontal respectively, the two principal components can be separately transmitted into the spectrograph. By maintaining the source of illumination steady, and adjusting the relative times of exposure for the two principal components so as to give equality of density on the photographic plate, their relative intensities can be measured. A consideration of Schwarzschild's constant is necessary for accurate values.

The liquids were studied in special double bulbs, and extreme purity of the liquid, especially freedom from floating dust particles, was ensured by repeated distillation in vacuum before an exposure was made. Otherwise there is in general a continuous spectrum of large intensity which is likely to affect the measurements appreciably.

Sources of Error.

There are various errors in the measurements on polarization, some of them very serious, which one has to guard against before the results can be relied upon. Among these comes, in the first place, the influence of the background illumination, which is in general unpolarized. In the present measurements, this illumination was completely avoided by making the bulb containing the liquid of very large capacity, usually of about 600 c.c. to 1000 c.c., the light from the walls of the vessels being thereby reduced to a minimum. As a further precaution, the whole bulb was thoroughly blackened except for a small entrance window and one for observation, and, in addition, a special horn of the usual shape also blackened completely was sealed to the back side of bulb so as to provide a cavity against which to view the track of light. The entire apparatus was shielded completely from the light of the arc by suitable screens of large dimensions, while the passage from the observation window of the bulb to the slit of spectroscope was completely enclosed.

The next source of error is the want of parallelism of the incident beam of light and the deviation of the direction of observation from the normal. As regards the first, the effective size of the mercury lamp was considerably reduced, with the help of an aperture, as also the aperture of the focussing lens. Sufficient care was also taken that the portion of the track in the liquid whose image is formed on the slit corresponds exactly to the focal plane of the condensing lens in the incident beam. Since at the focus the direction of the incident light deviates very little from

the axis, the small influence of the finiteness of the aperture of the condensing lens, which is already small, is completely eliminated. This point has been discussed at great length by Dr. I. R. Rao*, who adduces also extensive experimental evidence in its support.

The nicol used was of large size, and the length of the slit of the spectrograph was sufficiently reduced so as to allow only light which passed centrally through the nicol to enter the instrument.

Calibration of the Instrument.

Next, we consider the calibration of the spectrograph for the polarization induced by the various parts of the instrument, especially by the narrow metallic slit, and unequal loss of the two polarized components by oblique refraction at the two faces of the dispersing prism. For this purpose direct light from a distant source, which was tested and found to be perfectly unpolarized, was allowed to pass through the spectrograph, and the light emerging at the camera end of the spectrograph was analysed visually by the well-known method due to Cornu, with the help of a double-image prism and a nicol. The vertical component was much feebler than the horizontal, as we should expect, and their ratio did not vary appreciably with the wave-length for the region of the spectrum used in the measurements. Also, the calibration was repeated with the nicol placed immediately in front of the spectroscope slit, and taking a series of pairs of photographs, for one of which the axis of the nicol was vertical and for the other horizontal, the relative times of exposure for these two positions of the nicol being varied in the different photographs. The calibration of the instrument was carried out for both wide and narrow slits. Care was taken, of course, to keep the current through the mercury arc constant, and exposures were given only after allowing the arc to run for a sufficiently long time to attain a steady temperature.

Method of Measurement.

Having calibrated the instrument, the determination of the polarization of the light scattered by individual liquids is straightforward. As before, the relative times of exposure are adjusted for the two positions of the nicol so as to give equally intense lines. In the case of each liquid two determinations are made, one with a very narrow slit, which

* Ind. Journ. Phys. ii. p. 61 (1927).

gives the polarization of the scattered line of exactly the same frequency as the exciting line and isolated from rotational Raman frequencies which appear as wings on either side of this line. The second determination is made with a wide slit, which naturally gives the combined polarization of the unmodified line and the rotational wings accompanying it. The width of the slit is large enough to include the complete wings on either side of the central line. Of course the vibrational lines are too far away to be included even with the wide slit. The value for the depolarization factor, *i. e.*, the ratio of the intensity of the horizontal vibration in the scattered light to that of the vertical, is always greater in the case of the wide slit than with a narrow slit. This points to a large depolarization of the wings as compared with the central core.

Results.

The results obtained for incident unpolarized light and transverse observation are tabulated below. In the case of

TABLE I.

Depolarization factor in per cent.

Liquids.	Observed value.		Calculated value.	
	Total. scattering (wide slit).	Rayleigh scattering (narrow slit).	Classical theory (Maxwellian).	Quantum theory (spin-theory).
Benzene	42	33	16·6	32·1
Carbon disulphide	64	56	36·4	55·5
Toluene	45	37	18·6	35·0
Carbon tetrachloride ...	6	5	1·6	3·8
Phosphorus trichloride.	21	13	6·4	14·4

carbon disulphide, in order to avoid photochemical decomposition, only λ 4358 was filtered out from the mercury arc and used as the incident radiation. In the case of the other liquids the estimates are made for both λ 4046 and λ 4358 lines. The first column of figures gives the depolarization with a very wide slit, so that the Rayleigh and rotational Raman scattering are superposed. In the second column are given the values obtained using a very narrow slit, so that only the Rayleigh scattering is recorded on the plate

with the exposures given. The third column gives the values calculated on the basis of the classical or Maxwellian theories of light-scattering. The fourth column gives the theoretical values of the depolarization calculated on the theory of the spinning photon discussed recently by Prof. Raman and S. Bhagavantam.

Discussion of Results.

Theory of Light-Scattering.

Mention has already been made in an earlier part of the paper of the general theory of scattering by anisotropic molecules put forward by Lord Rayleigh and Born. In these theories the frequency of thermal rotation of the molecules is assumed to be negligible in comparison with that of the incident light, so that in effect the molecules are assumed to be non-rotating. Naturally, the scattered frequency comes out on the theory to be exactly the same as that of the incident, and no change of frequency is contemplated at all. However, as is now well known, accompanying the classically scattered line there is a wing extending on either side whose intensity is quite appreciable, which arises from the fact that the scattering molecules are rotating and are not stationary. That this view regarding the origin of these wings is correct can now be taken to be definitely established, since the structure of the wings can be followed up from the state of a gas where they are clearly resolved into discrete lines to gradually increasing densities of aggregation when the individual rotational lines broaden, until at densities even considerably lower than that of the liquid they merge into one another, forming a continuous band extending on either side of the central core. These lines correspond to changes in rotational energies of the molecules, their actual separation being also exactly the same, as we should expect from measurements on the band spectra of the molecules.

In view of the above facts, the treatment by Rayleigh has to be modified, so as to take into account the actual thermal rotation of the scattering molecules. A wave mechanical treatment has been given by Manneback * which takes this fact into consideration, and identical results have also been derived on the basis of purely classical considerations by Bhagavantam †, in a very much simpler manner. It is not necessary in this place to give an account of these treatments,

* *Zeits. f. Phys.* lxii. p. 224 (1930).
† Ind. Journ. Phys. vi. p. 331 (1931).

and we will merely content ourselves with quoting some of the results of these theories which are relevant for our present discussion.

Incident Polarized Light.

Let us consider a beam of plane polarized light of unit intensity travelling along the X axis, the direction of observation being along the Y axis of a rectangular system of coordinates. Considering the general case of a molecule, the contribution *per molecule* to the intensity of the scattered light along the Y axis is as follows:—

Considering, firstly, the core (corresponding to scattering of the same frequency as the incident light), the bulk of the intensity of its Z component can naturally be considered to arise from the molecule as though it had a mean polarizability $\mu = \frac{2A+C}{3}$, proportional to μ^2, and the remaining portion of the intensity of this component arises from the anisotropic nature of the molecules and is proportional to $1/45\ (C-A)^2$. As regards the intensity of the X component of the core, the whole of it arises only from the anisotropy of the molecules and is proportional to $1/60\ (C-A)^2$.

Regarding the intensity of the wings, the total intensity of the Z component (*i. e.*, integrated over the whole spectral range of the wings, extending on *both* sides of the core) comes out as proportional to $\frac{(C-A)^2}{15}$, while the aggregate intensity of the X component of the wings is proportional to $\frac{(C-A)^2}{20}$. Thus the depolarization of the transversely scattered light, defined in the usual way as the ratio of the intensity of the X component to that of the Z component, comes out as $\frac{1/60\ (C-A)^2}{\mu^2+1/45\ (C-A)^2}$ for the core alone, and as 3/4 for the wings alone, the value being independent of the particular spectral range inside the wing which we choose, and a value of $\frac{1/15\ (C-A)^2}{\mu^2+4/45\ (C-A)^2}$ for the core and the wings taken together. The total intensity of the core and wings together is proportional to $\mu^2+4/45(C-A)^2$ per molecule for the Z component and to $3/45(C-A)^2$ for the X component. These are exactly the same expressions as are derived on

the Rayleigh theory. This is in accordance with what we should expect in view of the fact that the expressions are independent of the rotational frequencies of the molecules, and in the limiting case, where the rotational frequency is negligible in comparison with the frequency of the incident light, Bhagavantam's results should obviously reduce to those of Rayleigh.

Incident Unpolarized Light.

If instead of the incident light being polarized, it is perfectly *unpolarized*, the corresponding changes in the expressions are easily derived, the results for this case being as below :—

Core.—Intensity of the Z component proportional to $\mu^2+7/180(C-A)^2$ per molecule and of the X component to $1/30(C-A)^2$.

Wings.—Intensity of the Z component proportional to $7/60(C-A)^2$ and of the X component to $1/10(C-A)^2$.

The total intensity of the core and wings taken together is proportional to $\mu^2+13/45(C-A)^2$, which is again the same expression as the one obtained on the basis of the Rayleigh theory.

As regards the depolarization factor ρ, for this case the values are as follows :—

1. Core. $$\rho_c = \frac{1/30(C-A)^2}{\mu^2+7/180(C-A)^2} \quad . \quad . \quad . \quad (1)$$

2. Wings. $$\rho_w = 6/7 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

3. Core and wings. $$\rho_{cw} = \frac{2/15(C-A)^2}{\mu^2+7/45(C-A)^2} \quad . \quad . \quad . \quad (3)$$

From (1) and (3) we get the following simple relation between the depolarization of the core alone, viz., ρ_c, and that of the core and wing together, viz., ρ_{cw},

$$\rho_c = \frac{2\rho_{cw}}{8-7\rho_{cw}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Extension of the Theory to Liquid State.

If the medium is not gaseous but is in the liquid state, the expressions for the intensity of the Z and X components of the wings, as also of the X component of the core, which arise from the anisotropy of the molecules and are

therefore directly proportional to the number of molecules, will still hold valid. In the Z component of the core also the expression for the anisotropic contribution to its intensity which is proportional to $(C-A)^2$ will be unaltered. The isotropic contribution to the intensity of the Z component of the core, however, which is proportional to μ^2, will no longer be valid, this term being now proportional not simply to μ^2 but to $KT\beta n\mu^2$, where K is the Boltzmann constant per molecule, T is the absolute temperature, β is the isothermal compressibility, and n is the number of molecules per unit volume of the medium. For the gaseous state, $KT\beta n$ would, of course, be unity.

The value of ρ_w will be the same as for a gas, viz., 6/7 due to the introduction of the new factor $KT\beta n$ multiplying μ^2; the value for ρ_w and ρ_{cw} will now be respectively,

$$\rho_c = \frac{1/30(C-A)^2}{KT\beta n\mu^2 + 7/180(C-A)^2}. \quad . \quad . \quad . \quad (5)$$

and

$$\rho_{cw} = \frac{2/15(C-A)^2}{KT\beta n\mu^2 + 7/45(C-A)^2}, \quad . \quad . \quad . \quad (6)$$

instead of equations (1) and (3).

Apart from the above considerations, it may also be noted here that, in extending the theory to the liquid state, a possible influence of the close packing of molecules on the intensity of the rotational Raman scattering has to be borne in mind. In the theory of intensity of the rotational Raman scattering by gases outlined above, it is assumed that the scattering particles—individual molecules in this case—are free to rotate, and so long as this condition is satisfied the rotational wings should be present with the requisite intensity, whatever may be the magnitude of the moment of inertia or the rotational frequency of the scattering particle. If, however, the scattering particle is so heavy and rotates, if it can rotate at all, with an extremely low frequency that for all practical purposes it may be regarded as stationary in the process of scattering, the above considerations will not be applicable. Such a circumstance can be expected to be present only in exceptionally viscous or highly associated liquids, where large molecular groups are presumably present. Fatty acids constitute typical examples of such a class of compounds, and it is interesting to note that, in spite of a high depolarization exhibited by them, the photographs of their scattered spectra seem to show no appreciable rotational wings. The cases of non-polar molecules such as benzene, carbon disulphide, carbon

tetrachloride, which are studied here may, however, be treated for this purpose in a manner similar to that of the gases.

Relation to actual Experimental Results.

Before proceeding to discuss how far the measurements on depolarization of the scattered lines with very narrow slit which gives the value for the core alone, viz., ρ_c, and for a very broad slit which gives ρ_{cw}, which are given in Table I., satisfy the relation (4), it may be of interest to discuss a few other important results which follow from the theory. In the first place the direct proportionality of the intensity of the wings to $(C-A)^2$, *i. e.*, to the magnitude of the optical anisotropy of the molecules given by the theory, is an experimental fact which has been reported previously. In the present observations also the intensity of these wings in the case of carbon-disulphide and liquids of the aromatic class which are highly anistropic is very conspicuous, while pentane, carbon tetrachloride, and other liquids which are feebly anisotropic present a striking contrast, the wings in these cases being only just detectable,

The polarization of these wings was directly measured in a number of cases. The following are the results obtained in two typical liquids :—

TABLE II.

Liquids.	Depolarization factor for the wings.
Benzene	0·8
Carbon disulphide	0·8

The values agree as closely with the theoretical value 6/7 (·86) as might be expected from the conditions of the experiment. It may be noted that the different parts of the wing are all polarized to the same extent in accordance with the theory.

Coming now to the relation between the values of ρ_c and ρ_{cw}, the values of ρ_c calculated from ρ_{cw} according to relation (4) are given in the third column of figures in Table I. It will be seen that the values of ρ_c so calculated are considerably smaller than the observed values given in the immediately preceding column of the same table. The large differences point unmistakably to some fundamental defect in the classical theory.

They receive, however, a natural explanation on the basis of the theory of the spinning photon recently suggested by Prof. Raman and Bhagavantam. The essential difference between the classical theory and the theory of the spinning photon arises in the following manner:—On the classical theory in any individual encounter between a rotating molecule and a linearly polarized photon, whatever the *sense* of rotation of the colliding molecule may be, there is an equal chance of the molecule gaining or losing energy. On the other hand, in the theory of the spinning photon a linearly polarized photon is conceived of as one having an equal chance of spinning one way or the other, and an attempt is made to conserve not only the energy but also the angular momentum in each individual encounter. It follows that if the photon happens to be spinning in the right-handed sense at the time of the collision and if the colliding molecule is also spinning in the same sense, then the transition in which the molecule loses energy is forbidden while the transition in which the molecule gains energy is permitted. In the same manner, if we consider the various possibilities of the relative spins of the colliding molecule and the photon at the instant of collision, it is easily seen that only half the number of transitions is allowed whereas the other half is forbidden. Thus the intensities of the wings will be only one-half of what we should expect on the classical theory, while the total intensity of the wing and the core, for either of the two principal components, viz., vibrations along the Z and the X axis, will be the same as on the classical theory.

The corresponding changes in the final expression for the intensities of the core and wings in either of the components are therefore as follows for incident unpolarized light:—

Wings.—Intensity of the Z component is proportional to $7/120(C-A)^2$.

Intensity of the X component is proportional to $1/20(C-A)^2$.

The corresponding value of the depolarization still remains as 6/7.

Core.—Intensity of the Z component is proportional to $KT\beta n\mu^2 + 7/72(C-A)^2$ and of the X component to $1/12(C-A)^2$.

The depolarization of the core ρ_c will be given by

$$\rho_c = \frac{1/12(C-A)^2}{KT\beta n\mu^2 + 7/72(C-A)^2} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Core and wings together.—The intensities of the Z and X components for the combined core and the wing will be the same as before, as also the values of ρ_{cw}.

As the new relation between ρ_c and ρ_{cw} we obtain, in place of (4),

$$\rho_c = \frac{10\rho_{cw}}{16-7\rho_{cw}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Thus while the spin theory gives, just as the classical theory, the observed depolarization of 6/7 for the wings alone, it gives for the relation between ρ_c and ρ_{cw} quite different expressions. The values of ρ_c calculated from ρ_{cw} on the basis of the above relation (8) given by the spin theory are given in the final column of Table I. These are in satisfactory agreement with the experimentally observed values, and the result must be taken to decide conclusively in favour of the spin theory as against the classical one given in an earlier part of this section. The case of carbon-tetrachloride is, however, interesting in that it does not show the diminution in polarization required even by the spin theory. The anomaly may in some manner be connected with the high symmetry of the molecule.

The author desires to thank Prof. Sir C. V. Raman, F.R.S., N.L., for his kind interest in the work.

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XXVII. *On the Fine Structure of the Arc Lines of Lead and Tin. By* S. B. L. Mathur, *M.Sc., Royal Institute of Science, Bombay* *.

SINCE the time Michelson [1] with the aid of his interferometer studied the structure of spectral lines, considerable advance has been made not only in the technique but also in the theory of the causes to which the complexity of structure is ascribed. Joos [2] and Ruark and Chenault [3] showed that fine structure of spectral lines is due to the fine structure of the spectral terms. A fine quantum number, f, was introduced to distinguish the various levels of a complex spectral term, and it was shown that in some cases this

* Communicated by the Author.

quantum number obeys the selection rule $\Delta j = \pm 1$ or 0. From the data of Back [4] and Wali Mohammad and the Author [5], Kimura [6] analysed a number of terms of thallium and explained the structure on the basis of the above considerations. Nagaoka, Sugiura, and Mishima [7] suggested that the hyper-fine structure of lines may be due to different isotopes, but this view meets with only a partial success. Complexity of structure is not confined to lines of elements which are mixtures of isotopes. Also, elements may be mixtures of a number of isotopes and yet be free from complexity of structure in their spectrum lines. It was Pauli [8] who suggested that the origin of the hyper-fine structures may be explained by assuming that the nucleus possesses angular momentum and magnetic moment. Goudsmit and Back [9] in their work on bismuth lines showed strong evidence in support of Pauli's hypothesis. Jackson [10] worked on the hyper-fine structure in the arc-spectrum of cæsium, and his analysis is in very satisfactory agreement with the work of Back and Goudsmit. But Pauli's hypothesis, even, may not be the final word on the subject as some difficulties confront us. Fine structures are quite capricious in their occurrence, and analogous elements do not have similar fine structures. As Schüler and Keyston [11] have pointed out, changes in the intensity of the hyper-fine structure of lines occur, and the effect may be real and not an instrumental error. Self-absorption of the light in the source is believed not to be the cause of these changes, and their origin remains completely unexplained. It is remarkable that the hyper-fine structure, which is due to the quantized spin of the atomic nucleus, should be so easily influenced by causes external to the atom.

The following work was undertaken in the hope of obtaining data for the elucidation of the causes of complexity ; and lead and tin were particularly chosen in view of their isotopic nature. While the work was in progress, the interesting paper of Wali Mohammad and Sharma [12] on the hyper-fine structure of lead was published, and it was with a sense of pleasure that the author found that the results obtained by him were not very different.

Experimental Procedure.

A specially made water-cooled arc-lamp working in vacuum was at first used. The two electrodes of carbon could be brought into contact with each other and then separated by means of an electromagnetic device. One of

the electrodes was, as usual, fed with the substance under investigation. But this arrangement was later on given up in favour of another with which the author had worked in collaboration with Dr. Wali Mohammad while at Lucknow University. A stream of electrons from a platinum oxy-cathode heated to incandescence by a current of 15 to 20 amperes was made, by means of an electric field obtained from 220 volt mains, to impinge upon the anode of the material under investigation. The thermionic current thus obtained varied from about 0·3 to 1·5 amp. in the case of lead to from about 0·5 to 3·5 amp. in the case of tin. Such a lamp has an immense advantage over others in the fact that the lines, being obtained in vacuum, are very sharp and the intensity can be controlled over a wide range. Self-reversals do not occur as readily as they do in an arrangement of the type with which the author worked at first.

The light from the source thus obtained was focussed on the slit of a Füess quartz spectrograph by means of an achromat of about 40 cm. focal length. The fine structure was obtained with the aid of a Lummer-Gehrcke plate supplied by Messrs. Adam Hilger & Co., and tested in the laboratory as regards its performance on the lines λ 4046 Å. and λ 4358 Å. of mercury.

Ilford Golden Iso-Zenith and Wellington spectrum plates were used for photographing the lines and their structure.

Von Baeyer has arrived at the following value of $\Delta_{\lambda_{max.}}$, the distance in Ångström units between the two successive orders of the fringe system of a line

$$\Delta\lambda_{max.} = \frac{n\lambda^2}{n^2\lambda - 4t^2\mu\frac{d\mu}{d\lambda}},$$

where n is the order of the fringe system and is given by

$$n\lambda = 2t\sqrt{\mu^2 - 1},$$

t is the thickness of the Lummer-Gehrcke plate (4·481 mm.), and μ is the refractive index of the material of the plate for wave-length λ.

Following Schrammen [13] and others, first a dispersion curve giving λ and μ for the Lummer plate was prepared from which the value of μ and $\frac{d\mu}{d\lambda}$ could be found for any wave-length; and then another curve giving $\Delta\lambda_{max.}$ for a number of wave-lengths was drawn. Such a curve was found to be sufficiently accurate for obtaining the values of $\Delta\lambda_{max.}$ for any wave-length.

Results on Lead lines.

1. 5201·65.—This line has been found simple by Janicki[14], but Wali Mohammad[15] finds a satellite at +0·063. The author has not been able to find any trace of complexity in the line.

2. 5005·62.—Along with Janicki, Lunelund[16], Wali Mohammad, and Wali Mohammad and Sharma, the author also finds it simple.

3. 4340·65.—Simple.

4. 4168·21.—Simple.

5. 4062·30.—Simple.

6. 4057·97.—Nutting[17], working with an ordinary arc of 3 amp., found this line as well as 6002 extremely broad and diffused with a trace of structure—2 or 3 components—superposed. With a current of 2 amp. and with an excess of silver to reduce the lead spectrum, both the lines were reduced to a single narrow structure with diffused edges. Janicki, Lunelund, Wali Mohammad, Mohammad and Sharma, and others have found two satellites in the line 4057·97. Their results, as well as those of the author, are tabulated below :—

Janicki.	Lunelund.	Mohammad.	Mohammad & Sharma.	Author.
	−0·092 (2)			
−0·041 (3)	−0·041 (2)	−0·041 (5)	+(?) 0·040 (4)	−0·040 (5)
0·000 (10)	0·000 (10)	0·000 (10)	0·000 (10)	0·000 (10)
+0·033 (2)	+0·034 (3)	+0·032 (5)	+ 0·034 (5)	+0·032 (7)

7. 4019·77.—Simple.

8. 3740·10.—Simple.

9. 3683·60.—Simple.

10. 3671·65.—Simple.

11. 3639·71.—Wali Mohammad and Sharma find the following structure for this line :—

−0·034 (3).
0·000 (10).
+0·027 (5).

The author finds the structure to be as follows :—

$-0{\cdot}048$ (5),
$0{\cdot}000$ (10),
$+0{\cdot}024$ (6).

Another satellite at $+0{\cdot}012$ may be present, but as its position falls contiguous to the main line fringe, it is difficult to say whether any such satellite is really occurring.

12. 3572·88.—Simple.

Results on Tin lines.

1. 5631·91.—Nutting finds this line to be narrow but with very diffuse edges. As the intensity is increased it broadens much more rapidly on the side of lesser wavelength, and, finally, a diffuse component splits off on this side just as the line goes over into a complete reversal.

The author finds the line simple. Narayan [18] also finds it so.

2. 4524·92.—According to Nutting this line also behaves in the same way as the above one. Wali Mohammad and also Narayan have found this line simple. The author also finds the same results.

3. 3801·16.—Simple.

4. 3655·88.—Simple.

5. 3330·71.—This line also comes out simple.

Thus a number of lines in the spectrum of lead have been examined, and except two, all of them show a remarkable simplicity of structure. Similarly, tin also reveals a lack of complexity in the few lines it emits in the region investigated. It will be of interest to recall here the work of Aronberg [19] and Merton [20] on the structure of $\lambda 4058$ of the isotopes of lead. Narayan, also working on similar ideas, failed to find any complexity in the lines $\lambda 5631$ and $\lambda 4524$ of tin.

The author would be failing in his duty if he did not here express his gratitude to Prof. Dr. Wali Mohammad, Dean of the Faculty of Science, University of Lucknow, under whose care and guidance he acquired the necessary technique and knowledge about the subject. It is a pleasure to him also to express thanks to Dr. T. S. Wheeler, Principal of the Royal Institute of Science, Bombay, for the kindly interest taken in the course of the work, and also to Mr. V. D. Mazmudar, M.Sc., for the assistance given.

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XXVIII. *The Heat of Formation of Nitrous Oxide.*

By T. Carlton Sutton, *M.A., M.Sc., F.Inst.P.**

Introduction.

THE heats of formation of the oxides of nitrogen as determined by Thomsen and by Berthelot are summarized in Table I. The agreement shown in the case of nitrous oxide is unsatisfactory. The heat of formation of nitrous oxide was obtained by Thomsen † by two methods. In one method nitrous oxide was burnt in hydrogen and the value, −18·01 Cal/mol, was deduced. In the other method, carbon monoxide was burnt in nitrous oxide and a somewhat lower value, −17·47 Cal/mol, was deduced. Berthelot ‡ measured the heats of explosion of carbon monoxide mixed with (1) pure oxygen, (2) nitrous oxide. From this he deduced

* Communicated by the Author.
† Thomsen, 'Thermochemie,' ii. p. 192, diagram.
‡ Berthelot, 'Thermochemie,' ii. p. 102.

the value, $-20{\cdot}6$ Cal/mol, for the heat of formation of nitrous oxide.

In the present measurements use has been made of an apparatus of high sensitivity developed in connexion with the calorimetry of cordite, and suitable for the explosion of gases at high pressures. Nitrous oxide has been exploded with excess of hydrogen * in accord with the reaction :

$$H_2 + N_2O \rightarrow H_2O + N_2.$$

From this the value $-20{\cdot}5 \pm 0{\cdot}3$ Cal/mol has been obtained for the heat of formation of nitrous oxide.

TABLE I.

Body.	Formula.	Heat of formation (Cal/mol).	Remarks.
Nitrous oxide	N_2O	$-17{\cdot}7$	Thomsen.
		$-20{\cdot}6$	Berthelot.
Nitric oxide	NO	$-21{\cdot}6$	Thomsen.
		$-21{\cdot}6$	Berthelot.
Nitrogen peroxide	N_2O_4	$-2{\cdot}6$	Thomsen.
		$-2{\cdot}2$	Berthelot.
do. (at 200° C.) ...	NO_2	$-7{\cdot}9$	Berthelot.
Nitrogen pentoxide	N_2O_5	$-1{\cdot}2$	Berthelot.

Sensitivity of the Method.

Prolonged experience in the calorimetry of cordite has shown that the energy emitted under these conditions can be measured to within 1 part in 1000. The heat associated with the above equation is approximately 88 Cals per mol of nitrous oxide, and the error is, therefore, less than 0·1 Cal/mol, or about 1 part in 200 on the deduced heat of formation of nitrous oxide.

Measurement of the mass of reacting gas involves more error than the thermal measurements. The following three methods of measurement have been available, two of which have been employed :—

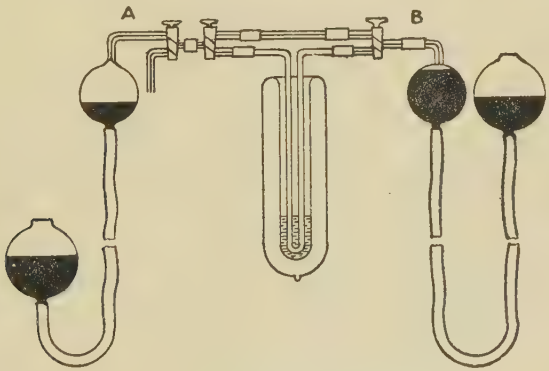
(1) By means of a high-grade balance, the weight of nitrous oxide has been measured to $\pm 0{\cdot}017$ grams (see Table III.). This corresponds with an error of 0·29 Cal/mol in the heat of formation.

* A suitable supply of carbon monoxide at high pressure was not available.

(2) The total nitrogen in the products has been measured to 1 part in 300 (see Tables V. and VI.). This corresponds with an error of 0·30 Cal/mol in the heat of formation. Measurement of the total volume of the gases left after explosion is the chief source of error.

(3) The water formed in the explosion could have been measured ; this, however, was not done since the error involved was of the order of 1 part in 200 and corresponded with 0·4 Cal/mol in the heat of formation.

No useful purpose is served by measuring the mass of the hydrogen, which is added in excess.



Purity of the Nitrous Oxide.

The cylinder of nitrous oxide was obtained from Messrs. Coxeter, London. This cylinder was stood on end in a cradle. A few litres were blown off so as to expel such impurities as had collected at the top. The exit was then closed and the cylinder allowed to stand. At intervals it was struck and shaken, so that bubbles tended to collect at the top. On the following day the cock was again opened and more gas blown off. This procedure was repeated. The composition of samples of gas taken from the cylinder after this preliminary treatment was found to be regular, the impurities being oxygen and nitrogen in the proportion of one to nine.

Analysis of mixtures containing nitrous oxide is difficult on account of the solubility of the gas in both aqueous and

alcoholic reagents, its inert nature, and the lack of a specific solvent. The following method was adopted :—

A slow stream of gas from the cylinder was passed directly through drying tubes and found to be dry. A sample of 150 c.c. of the gas was then condensed with liquid air in the apparatus shown in the figure. By successive evacuations by means of the bulb A, the uncondensed residue was removed, and was passed into the collecting vessel B. 2·75 c.c. of residual gas were collected in this way and analysed in a micro-apparatus developed in this laboratory *.

The composition by volume of the gas from the cylinder was thus found to be :

Nitrous oxide	98·17	per cent.
Nitrogen	1·65	,,
Oxygen	0·18	,,

Purity of the Hydrogen.

A sample of the hydrogen was analysed by methods recently developed here † for the estimation of small quantities of oxygen and for the direct measurement of nitrogen. The composition by volume was found to be :

Hydrogen	98·45	per cent.
Oxygen	0·18	,,
Nitrogen	1·37	,,

Filling of the Closed Vessel.

The closed vessel, which had a volume of 150 c.c., was evacuated, filled with hydrogen to approximately 30 atmospheres, and weighed. It was then further filled with nitrous oxide, care being taken that the quantity of hydrogen considerably exceeded the quantity of nitrous oxide. The vessel was again weighed.

The precision of these weighings limits the accuracy of the measurements and is therefore discussed in detail.

The Balance.

This instrument was made by de Grave of London and may be used with weights up to 50 kilograms. The

* Ambler, 'Analyst,' liv. p. 517 (1929).

† Ambler, 'Analyst,' lv. p. 677 (1930), and lvi. p. 804 (1931).

weight of the closed vessel used for these measurements is $9\frac{1}{4}$ kilograms.

The sensitivity for such loads is shown in Table II.

TABLE II.

Sensitivity of de Grave Balance.

Left-hand pan.	Right-hand pan.	Mid-point of swing of pointer.
	gm.	
Closed vessel and fittings.	9242·55	Zero.
,, ,,	9242·60	0·8 divisions left.
,, ,,	9247·55	0·5 divisions left.
,, ,,	9247·50	0·5 divisions right.
,, ,,	9242·05	0·7 divisions right.
,, ,,	9242·10	Zero.
,, ,,	9239·35	Zero.
,, ,,	9239·40	0·9 divisions left.
,, ,,	9244·55	0·5 divisions right.
,, ,,	9244·60	0·3 divisions left.

The sensitivity varies from 0·7 to 1·0 divisions per 0·05 gm. The mid-point of the swings can be determined to 0·1 division. A difference of weight of 0·01 gm. would therefore be shown clearly.

A further error is introduced by changes in the zero of the balance. The extent of this error depends on the condition of the balance at the time of weighing. As this is difficult to control, measurements of the change in zero have been made at each weighing.

TABLE III.

Determination.	Weight of nitrous oxide.	Zero.	Remarks.
P.			
Bomb filled with hydrogen.	Before weighing (arms equally weighted).	+0·3	Whence, weight
	Bomb left, 9242·05 right.	+0.7	=9242·11$_4$
	Bomb left, 9242·10 right.	0·0	±0·036 gm.
	After weighing (arms equally weighted).	−0·7	

TABLE III. (*con.*).

Determination.	Weight of nitrous oxide.	Zero.	Remarks.
P.			
Bomb filled with hydrogen and nitrous oxide.	Before weighing (arms equally weighted).	−0·7	Whence, weight
	Bomb left, 9249·50 right.	+0·1	$=9249{\cdot}55_6$
	Bomb left, 9249·55 right.	−0·7	$\pm 0{\cdot}006$ gm.
	After weighing (arms equally weighted).	−0·9	
Weight of gas added $=7{\cdot}44_2 \pm 0{\cdot}042$ gm.			
Weight of nitrous oxide (98·8 per cent.) $=7{\cdot}35_2 \pm 0{\cdot}042$ gm.			
Q.			
Bomb filled with hydrogen.	Before weighing (arms equally weighted).	−0·3	Whence, weight
	Bomb left, 9239·40 right.	−0·9	$=9239{\cdot}37_8$
	Bomb left, 9239·35 right.	0·0	$\pm 0{\cdot}011$ gm.
	After weighing (arms equally weighted).	−0·7	
Q.			
Bomb filled with hydrogen and nitrous oxide.	Before weighing (arms equally weighted).	−0·6	Whence, weight
	Bomb left, 9244·55 right,	+0·5	$=9244{\cdot}61_3$
	Bomb left, 9244·60 right.	−0·3	$\pm 0{\cdot}006$ gm.
	After weighing (arms equally weighted).	−0·4	
Weight of gas added $=5{\cdot}23_5 \pm 0{\cdot}017$ gm.			
Weight of nitrous oxide (98·8 per cent.) $=5{\cdot}17_2 \pm 0{\cdot}017$ gm.			

The determination Q is more reliable than the determination P.

Ignition.

A strand of cordite, Mk. I., size $3\frac{3}{4}$, weighing 0·012 gm., wrapped on platinum wire of diameter 0·012 cm., was used to ignite the mixed gases. The energy supplied to the platinum wire does not exceed 0·2 cal and is negligible in comparison with a total energy of the order of 10,000 cals. The correction to be applied for the decomposition of the cordite is 15 cals.

Calorimetry.

As mentioned above, the apparatus used was developed in connexion with the calorimetry of cordite. The accuracy of this apparatus has been found in practice to be limited by the temperature measurements. These were made by means of mercury-in-glass thermometers of the type developed in this laboratory. The degree of accuracy of the thermometers has already been discussed *.

A record of the calorimetric readings for the determination Q is given in Table IV.

TABLE IV.

Date, 25.3.31.

Bomb, Mark XVI. Calorimeter, 84.

Time.	Thermometer L.	Thermometer N.	Temp. Room.	Temp. Bath.	Stirring shaft r.p.m.
P.M.			19·5	22·1	180
3·6	18·481° C.	18·441° C.			
3·8	18·496	18·556			
3·12	18·527	18·586			
3·13	18·534	18·593			
3·14	18·541	18·600			
3·15½	Fired.	—			
			20·0	22·1	180
3·31	21·276	21·373			
3·35	21·283	21·381			
3·39	21·290	21·388			
3·42	21·295	21·394	19.8		180
3·49	21·309	21·407			
3·17½	21·253	21·346			
	18·567	18·623			
Difference.	2·686	2·724			
	0·044	0·002	Calibration correction.		
Rise.	2·730° C.	2·726° C.			

Mean, 2·728° C.

* Sutton, Journ. Sci. Instr. viii. p. 98 (1931).

Nitrogen Liberated in the Explosion.

The products of explosion and the amount of nitrogen liberated in the explosion are detailed in Tables V. and VI.

TABLE V.

Products of Explosion (determination Q).

Volume of gaseous products		3960±12 c.c.
Composition of gaseous products	nitrogen	68·0±0·1 per cent.
	hydrogen	31·9 per cent.
Water		2·111 gm.
Ammonia		0·004 gm.

TABLE VI.

Nitrogen Liberated by the Explosion (determination Q).

Initial nitrogen (free):	
(i.) from hydrogen cylinder	0·000,8 mol.
(ii.) from nitrous oxide cylinder	0·002,0 mol.
(iii.) from igniter	(negligible)
Total	0·002,8 mol.
Final nitrogen:	
(i.) free, 68 per cent. of volume of gaseous products	0·120,1 mol.
(ii.) ammonia	0·000,1 mol.
Total	0·120,2 mol.
Whence,	
Nitrogen from explosion	0·117,4 mol.
Estimated error of measurement (see Table V.)	0·000,4 mol.

Minor Reactions.

In Table VII. the effect of the minor reactions is detailed, and values are deduced for the energy emitted by the main reaction,

$$N_2O + H_2 \rightarrow N_2 + H_2O \text{ (liquid)}.$$

TABLE VII.

Energy Emitted on Explosion.

	Determination P.	Determination Q.
Rise in temperature	3·896° C.	2·728° C.
Water equivalent	3822 gm.	3822 gm.
Energy (measured)	14890 cal.	10425 cal.
Free oxygen (initial):		
(i.) from hydrogen cylinder	0·000,31 mol.	0·000,10 mol.
(ii.) from nitrous oxide cylinder	0·000,30 mol.	0·000,22 mol.
Total	0·000,61 mol.	0·000,32 mol.
Corresponding energy of combustion	85 cal.	43 cal.
Ammonia in products	5·35 milligrams.	4·00 milligrams.
Corresponding energy of formation	4 cal.	3 cal.
Correction for igniter (cordite)	15 cal.	15 cal.
Energy due to reaction: $N_2O+H_2 \rightarrow N_2+H_2O$ (liquid)	14·785±15 Cal.	10,365±10 Cal.

The Main Reaction.

In Table VIII. are collected from previous tables, (i.) the energies evolved by the main reaction, and (ii.) the reacting masses of nitrous oxide.

Three values are obtained for the measured molecular heat of reaction at constant volume. These values are in agreement within the limits of measurement, the magnitude of which has been detailed in each case.

The energy of the reaction has been taken as 88·3 Calories per mol at constant volume under the conditions of the measurement. The error does not exceed one part in three hundred.

Deviation from Simple Gas Laws.

Since nitrous oxide is highly compressible, and deviates materially from the simple gas laws, the usual difference of RT Cal/mol for each change of one mol in the gaseous

Table VIII.

The Reaction $N_2O + H_2 \rightarrow N_2 + H_2O$ (liquid).

	Determination P.	Determination Q.
Heat evolved on explosion at constant volume (Table VII.)	14·785 ±0·015 Cal.	10·365 ±0·010 Cal.
Mass of nitrous oxide (by weight) (Table III.)	$7{\cdot}35_2$ ±0·042 gm. $=0{\cdot}167_1 \pm 0{\cdot}000_9$ mol.	$5{\cdot}17_2$ ±0·017 gm. $=0{\cdot}117_5 \pm 0{\cdot}000_4$ mol.
Whence, Energy of reaction at constant volume	88·5 ±0·50 Cal/mol.	88·2 ±0·29 Cal/mol.
Mass of nitrous oxide (calc. from nitrogen produced on explosion) (Table VI.)	—	$0{\cdot}117_4 \pm 0{\cdot}000_4$ mol.
Whence, Energy of reaction at constant volume	—	88·3 ±0·32 Cal/mol.

reactants, cannot be applied in this case to deduce the heat of reaction at constant pressure from the heat of reaction at constant volume. In Table IX. is detailed the energy associated with the changes in the pressures of the reactants.

Table IX.

Energies of Compression of Reactants (determination Q).

	Mass.	Product PV at 20° C.	Remarks.
Initial:	mols.	Calories.	
Nitrous oxide.....	0·1174	$0{\cdot}1062 \times 0{\cdot}58$	At 17·5 atmospheres the value of the product PV for nitrous oxide is 0·904 times that for a perfect gas.
Hydrogen	0·1740	$0{\cdot}1740 \times 0{\cdot}58$	
Nitrogen.....	0·0028	$0{\cdot}0028 \times 0{\cdot}58$	
Total	0·2942	$0{\cdot}2830 \times 0{\cdot}58$	

TABLE IX. (*con.*).

	Mass.	Product PV at 20° C.	Remarks.
Final:			
Nitrous oxide	Nil.	Nil.	
Hydrogen	0·0566	0·0566×0·58	
Nitrogen	0·1202	0·1202×0·58	
Total	0·1768	0·1768×0·58	
Difference	0·1174	0·1052×0·58	
Whence,			
Difference between energy of reaction (Cp) and (Cv).	1·0	0·52	

Summary.

The molar energies of the reactions involved in the determination of the heat of formation of nitrous oxide are given in Table X.

TABLE X.

Reaction.	Molar energy (15° Calories).	
$N_2O+H_2 \rightarrow N_2+H_2O$ (liq.) ...	88·30 Cal.	Const. vol. (as measured).
	88·82 Cal.	Const. press. (see Table IX.).
$H_2+\frac{1}{2}O_2 \rightarrow H_2O$	68·31 Cal.	Const. press. (Rossini, Bureau of Standards, Journ. Research, vi. p. 1 (1931)).
Whence,		
$N_2O \rightarrow N_2+\frac{1}{2}O_2$	20·51 Cal.	
i. e. Heat of formation of nitrous oxide	−20·51 Cal/mol.	

The value −20·5 Calories per mol is therefore put forward as the heat of formation of nitrous oxide, and is considered accurate to within 0·3 Calories.

Research Department, Woolwich.
Feb. 4, 1932.

XXIX. *The Band Spectra of Zirconium Oxide.* *By* L. W. Johnson, *M.A., University of London, King's College* *.

IN 1910 Eder and Valenta † published the wave-lengths of about thirty band heads attributed to zirconium oxide, and they assigned these to some seven groups. These are, in fact, sequences of two different systems and reference is made to the (0, 0) band of a third system. A detailed measurement and vibrational analysis of this spectrum was thought to be desirable, and for this purpose good plates were obtained in the first order of a 21 ft. grating over the range λλ 4000–7000 which appears to be that covering the whole spectrum. While the measurement and analysis of these were in progress a paper appeared by F. Lowater ‡ giving these data from plates taken on a glass Littrow spectrograph, and in the first and second orders of a 10 ft. grating. In the same paper a complete analysis was made into three systems: $^3\Sigma \rightarrow {}^3\Pi$ in the red region, $^3\Sigma \rightarrow {}^3\Pi$ in the yellow region, and $^3\Pi \rightarrow {}^3\Pi$ in the blue region. Our own results were substantially in agreement with this analysis, and it would seem unnecessary to cover this ground further. Our wave-lengths were for the strongest band heads the average of three independent grating plates, and in the case of the weaker bands of two Littrow prism plates, and it may seem worth while to record these data together with a few remarks about the systems in question. The bands were produced in a carbon arc packed with zirconium oxide and burning 10–15 amps. As far as possible the flame mantle surrounding the arc was used, this being found freer from continuous spectrum and lines. The vibrational assignment in the following Table is that of Lowater. In a few cases it has been possible to classify additional members.

Table.

λ.	Int.	$\nu_{vac.}$	Assignment.
4168·89	(1)	23980·5	a 3,0 R_b
4195·81	(1)	23826·6	a 4,1 R_c
4313·26	(1)	23177·8	a 2,0 R_b
4321·09	(1)	23135·9	a 3,1 R_a
4337·55	(2)	23048·0	a 3,1 R_b

* Communicated by the Author.

† *Sitz. K. Akad. Wien.* abt. II. *a*, cxix. (1910).

‡ Proc. Phys. Soc. xliv. p. 51 (1932).

TABLE (*cont.*).

λ.	Int.	$\nu_{vac.}$	Assignment.	
4364·38	(1)	22906·3	a 4,2 R_c	
4369·13	(1)	22881·5	a 5,3 R_a	
4386·44	(1)	22791·2	a 5,3 R_c	
4469·61	(4)	22367·1	a 1,0 R_b	
4471·61	(10)	22357·0	a 1,0 R_c	
4503·87	(1)	22196·9	? a 3,2 R_a	
4519·57	(5)	22119·8	a 3,2 R_b	
4521·47	(5)	22110·5	a 3,2 R_c	
4619·80	(8)	21639·9	a 0,0 R_a	
4637·76	(20)	21556·1	a 0,0 R_b	
4640·56	(16)	21543·1	a 0,0 R_c	
4644·80	(7)	21523·0	a 1,1 R_a	
4663·17	(5)	21438·7	a 1,1 R_b	
4665·28	(4)	21428·9	? a 1,1 R_c	
4673·42	(6)	21391·7	a 2,2 R_a	
4716·82	(4)	21194·9	a 3,3 R_c	
4827·40	(5)	20709·3	a 0,1 R_a	
4847·13	(9)	20625·0	a 0,1 R_b	
4850·06	(8)	20612·6	a 0,1 R_c	
4873·92	(2)	20511·7	a 1,2 R_b	
4876·16	(1)	20502·2	? a 1,2 R_c	
			β 3,0 R_a	
4880·63	(7)	20483·5	? a 2,3 R_a	
			? β 3,0 X_a	
4899·71	(3)	20403·7	a 2,3 R_b	
4902·43	(4)	20392·4	a 2,3 R_c	
4925·80	(3)	20295·6	a 3,4 R_b	
4938·25	(4)	20244·4	? β 3,0 X_b	
5052·91	(3)	19785·1	a 0,2 R_a	
5073·96	(4)	19703·0	a 0,2 R_b	
5078·29	(8)	19686·1	? a 1,3 R_a	
5103·80	(2)	19587·8	a 1,3 R_c	
5126·65	(2)	19500·5	? a 2,4 R_b	
5145·40	(2)	19429·5	β 2,0 R_b	
5148·80	(2)	19416·6	β 2,0 X_b	
5184·97	(20)	19281·2		
5212·17	(6)	19180·5		
5224·28	(6)	19136·1	β 2,0 X_c	
5240·30	(2)	19077·6		
5304·59	(4)	18846·4	β 1,0 R_a	
5305·91	(8)	18841·7		
5308·37	(4)	18832·9	β 1,0 X_a	
5332·35	(6)	18748·3	β 2,1 R_a	
5333·57	(2)	18743·9		
5335·42	(4)	18737·5	β 2,1 X_a	
5349·50	(9)	18688·2	? a 1,4 R_b	
5360·38	(6)	18650·2	β 3,2 R_a	

TABLE (*con.*).

λ.	Int.	$\nu_{vac.}$	Assignment.		
5361·88	(6)	18645·0			
5375·71	(6)	18597·0		β 1,0 R_b	
5403·75	(4)	18500·5			
5404·30	(4)	18498·7		β 2,1 R_b	
5407·10	(6)	18489·1		β 2,1 X_b	
5432·70	(2)	18401·9			
5433·17	(5)	18400·4		β 3,2 R_b	
5436·86	(6)	18387·9		β 3,2 X_b	
5446·52	(1)	18355·3		? β 6,5 R_a	
5456·45	(4)	18321·8		β 1,0 R_c	
5461·55	(2)	18304·7		β 1,0 X_c	
5462·20	(2)	18302·6		β 4,3 R_b	
5465·04	(1)	18293·1		β 4,3 X_b	
5485·74	(4)	18224·0		β 2,1 R_c	
5491·40	(2)	18205·3		β 5,4 R_b	
5545·28	(8)	18028·4		β 4,3 R_c	
5551·71	(10)	18007·5		β 0,0 R_a	
5553·11	(10)	18003·0			
5556·28	(12)	17992·7		β 0,0 X_a	
5566·95	(2)	17958·2	α 0,4 R_a		γ 3,0 X_c
5575·91	(1)	17929·3		β 5,4 R_c	
5580·08	(6)	17915·9		β 1,1 R_a	
5581·55	(6)	17911·2			
5595·74	(4)	17865·8	? α 0,4 R_c		γ 4,1 R_c
5610·01	(4)	17820·4		β 2,2 R_a	
5628·95	(12)	17760·4		β 0,0 R_b	γ 5,2 R_c
5629·47	(12)	17758·7			
5633·91	(10)	17744·8		β 0,0 X_b	γ 2,0 R_a
5658·11	(8)	17668·9		β 1,1 R_b	
5658·55	(8)	17667·5			
5662·71	(4)	17654·5		β 1,1 X_b	
5688·12	(12)	17575·6		β 2,2 R_b	
5692·44	(8)	17562·3		β 2,2 X_b	
5718·15	(20)	17483·3		β 0,0 R_c	
5723·87	(16)	17465·9		β 0,0 X_c	
5735·68	(13)	17429·9			γ 2,0 X_b
5748·21	(16)	17391·9		β 1,1 R_c	
5753·86	(8)	17374·8		β 1,1 X_c	
5778·45	(12)	17300·9		β 2,2 R_c	
5783·98	(6)	17284·4		β 2,2 X_c	
5809·10	(8)	17209·6		β 3,3 R_c	
5814·39	(4)	17194·0		β 3,3 X_c	
5835·16	(4)	17132·7			γ 2,0 R_c

TABLE (*con.*).

λ.	Int.	$\nu_{vac.}$	Assignment.	
5839·79	(4)	17119·2	β 4,4 R_c	
				γ 2,0 X_c
5916·43	(4)	16897·4		γ 1,0 R_a
5947·01	(6)	16810·5		γ 2,1 R_a
5977·75	(8)	16724·1		γ 3,2 R_a
5983·74	(2)	16707·3		γ 3,2 X_a
5999·50	(2)	16663·5	β 2,3 R_b	
6008·53	(6)	16638·4		γ 4,3 R_a
6021·36	(8)	16603·0		γ 1,0 R_b
6027·10	(3)	16587·1		γ 1,0 X_b
6039·15	(6)	16554·0	β 0,1 R_c	
				γ 5,4 R_a
6053·86	(10)	16513·8		γ 2,1 R_b
6069·92	(4)	16470·1	β 1,2 R_c	
				γ 6,5 R_a
6086·74	(6)	16424·6		γ 3,2 R_b
6099·78	(4)	16389·5	β 2,3 R_c	
6120·06	(6)	16335·2		γ 4,3 R_b
6132·10	(1)	16303·1	β 3,4 R_c	
6136·90	(4)	16290·4		γ 1,0 R_c
6153·82	(6)	16245·6		γ 5,4 R_b
6170·20	(6)	16202·5		γ 2,1 R_c
6203·96	(10)	16114·3		γ 3,2 R_c
6215·78	(2)	16083·7	β 0,3 R_a	
6229·36	(20)	16048·5		γ 0,0 R_a
6235·23	(8)	16033·5		γ 0,0 X_a
6260·96	(14)	15967·6		γ 1,1 R_a
6266·52	(6)	15953·4		γ 1,1 X_a
6272·94	(4)	15937·1		γ 5,4 R_c
6292·72	(12)	15887·0		γ 2,2 R_a
6298·86	(4)	15871·8		γ 2,2 X_a
6312·56	(1)	15837·1	β 1,3 R_b	
				? γ 6,5 R_c
6324·39	(8)	15807·4		γ 3,3 R_a
6344·89	(20)	15756·4		γ 0,0 R_b
6351·12	(10)	15740·7		γ 0,0 X_b
6378·35	(18)	15673·7		γ 1,1 R_b
6384·48	(4)	15658·7		γ 1,1 X_b
6393·87	(4)	15635·7		γ 5,5 X_a
6412·25	(12)	15590·9		γ 2,2 R_b
6418·73	(2)	15575·1		? γ 2,2 X_b
6446·44	(6)	15508·2		γ 3,3 R_b
6451·77	(1)	15495·3		γ 3,3 X_b
6473·62	(20)	15443·0		γ 0,0 R_c
6480·54	(6)	15426·6		γ 0,0 X_c
				γ 4,4 R_b
6507·99	(14)	15361·5		γ 1,1 R_c

TABLE (*con.*).

λ.	Int.	$\nu_{vac.}$	Assignment.
6514·75	(4)	15345·5	γ 1,1 X_c
			γ 5,5 R_b
6542·72	(10)	15280·0	γ 2,2 R_c
6549·59	(2)	15263·9	γ 2,2 X_c
			γ 6,6 R_b
6578·94	(6)	15197·9	γ 3,3 R_c
6613·00	(1)	15117·6	γ 4,4 P_c
			γ 0,1 R_a
6644·77	(1)	15045·3	γ 1,2 R_a
6649·44	(1)	15034·7	γ 5,5 R_c
6677·90	(2)	14970·6	γ 2,3 R_a
6742·36	(2)	14827·5	γ 4,5 R_a
			γ 0,1 R_b
6777·00	(1)	14751·7	γ 5,6 R_a
			γ 1,2 R_b
6812·30	(1)	14675·3	γ 2,3 R_b
6847·30	(1)	14600·3	γ 3,4 R_b
6887·57	(1)	14514·9	γ 0,1 R_c
6923·69	(1)	14439·2	γ 1,2 R_c
6931·75	(1)	14422·4	γ 1,2 X_c
6960·05	(1)	14363·8	γ 2,3 R_c

Remarks.

The very unequal character of the intervals between the three heads of each band of the $^3\Pi \rightarrow {}^3\Pi$ system is remarkable, and at first sight casts some doubt upon the correctness of identification of the least refrangible head, more especially as it is only clearly observed in the (0, 0) band. If this is not, however, the third member of the triplet, there is at any rate no other head which might fill this rôle. Assuming the identification to be correct the separations of the components of the lower $^3\Pi$ level are $\nu\nu$ 292 and 313 and of the upper level they are $\nu\nu$ 208 and 300, showing a notable shift of the lower component towards the other two. This is in contrast with the corresponding intervals in the TiO molecule (which is the higher homologue of the ZrO molecule). These are, for the lower $^3\Pi$ level $\nu\nu$ 66·4 and 75, and for the upper $^3\Pi$ level $\nu\nu$ 64·5 and 66·2, the approximate equality being preserved.

The heads designated X by Lowater (*vide* Table) must be either P or Q heads presumably, and in the paper cited it is suggested that they may be the former. We incline, however, to regard them as Q heads in view of the fact that on

theoretical grounds strong Q branches are to be expected. If they are Q branches the Q–R interval should be approximately the same in both the $^3\Sigma \rightarrow {}^3\Pi$ systems, since the vibration frequencies in the two $^3\Sigma$ levels are very close. This is approximately true.

In the Table we have not included a large amount of band material which it has not been possible to fit into one of the three systems. We have found in some cases fragmentary data suggesting faint satellite heads attached to some of the main heads in the yellow system. As examples we give the following:

18007·5	17915·9	18846·4	18748·2	18650·2
18003·0	17911·2	18841·7	18743·9	18645·0

If they are genuine branches they may possibly be interpreted as ^RQ in type.

There is some evidence of the existence of another system, hitherto unrecorded, with its (0, 0) band at λ 5184·97. This also is degraded to the red side. A head at λ 5212·17 is probably the (1, 1) band and a head at λ 5240·3, possibly (2, 2), but our data are very incomplete.

XXX. *Interconversion Factors for Numbers in Energetic and Related Units. By* C. H. Douglas Clark, *M.Sc., A.R.C.S., D.I.C., Assistant Lecturer in Chemistry in the University of Leeds* *.

1. *Introductory Note on Units.*

IT has become customary in actual practice to quote energy values in a variety of different ways. A given amount of energy, in accordance with classical conceptions, may be expressed by means of different numbers, according as electrical, mechanical, thermal . . . energy is considered. Further, the employment of related units, not possessing the dimensions of energy, but capable of derivation from the older units by means of terms involving fundamental physical constants, has become quite general since the advent of new quantum and relativistic developments. The conversion of numbers between these systems enters into many types of practical work and calculation. The purpose of the present paper is to present a table which has been found convenient in actual cases. It is necessary to give a short introductory account of the units which are taken into consideration.

* Communicated by Prof. R. Whiddington, D.Sc., F.R.S.

Considering electrical units, difficulty is often experienced on account of three systems in use: electromagnetic, practical, and electrostatic. The international system of units differs but little from the practical system, and the two may be taken as identical for the present purpose, where four significant figures in each factor only are taken into account The accuracy with which the fundamental constants are known does not justify a greater degree of approximation than this. Now, as is well known, Coulomb's laws of magnetic and electrostatic attraction assume the same general forms, but involve different constants, the magnetic permeability and the specific inductive capacity respectively. The

Table I.

Interconversion Factors for Numbers expressing Quantity (or Charge) in Different Units.

Q_m electromagnetic units	$Q_m = \frac{1}{10} Q$	$Q_m = \frac{1}{c} Q_s$ $(c^{-1} = 3{\cdot}336 \times 10^{-11})$
$Q = 10 Q_m$	Q coulombs	$Q = \frac{10}{c} Q_s$ $(10c^{-1} = 3{\cdot}336 \times 10^{-10})$
$Q_s = cQ_m$ $(c = 2{\cdot}998 \times 10^{10})$	$Q_s = \frac{c}{10} Q$ $(10^{-1}c = 2{\cdot}998 \times 10^{9})$	Q_s electrostatic units

units of electrical quantity in the electromagnetic and electrostatic systems are defined in the same way (quantity which when placed 1 cm. from an equal like quantity repels it with a force of 1 dyne), but, equating the dimensions in the two cases, it is found that the ratio between the units has the dimensions of a velocity, which, according to the electromagnetic theory of light, may be equated to the velocity of light *in vacuo* (here denoted by c). The practical unit (coulomb) is derived from the electromagnetic unit by dividing by 10. The conversion factors for quantity (or charge) are therefore as shown in Table I.

Potential difference (or E.M.F.) is next considered in terms of the three systems of units, the definition of the unit in the electromagnetic system taking the same form as in the electrostatic system (unit potential difference exists between two points when the work done in taking unit quantity from one point to the other is 1 erg). The practical

unit (volt) is then derived from the electromagnetic unit by multiplying by 10^8. The factor in the case of the international volt is $1{\cdot}0005 \times 10^8$, so that for the present purpose either unit may be employed in the conversion tables within the limits of accuracy of the calculations. The corresponding table for E.M.F. is given as Table II. below.

It will be noted that the quantities considered in Tables I. and II. are directly measurable. It becomes possible to find the corresponding conversion factors suitable in other cases by means of simple well-known relations (for example, energy = quantity × E.M.F., capacity = quantity/potential and so on). In the practical system, the unit of energy

TABLE II.

Interconversion Factors for Numbers expressing Electromotive Force (or Potential) in Different Units.

$\mathbf{V}_m$ electromagnetic units	$\mathbf{V}_m = 10^8\mathbf{V}$	$\mathbf{V}_m = c\mathbf{V}_s$ $(c = 2{\cdot}998 \times 10^{10})$
$\mathbf{V} = 10^{-8}\mathbf{V}_m$	$\mathbf{V}$ volts	$\mathbf{V} = \frac{c}{10^8}\mathbf{V}_s$ $(10^{-8}c = 299{\cdot}8)$
$\mathbf{V}_s = \frac{1}{c}\mathbf{V}_m$ $(c^{-1} = 3{\cdot}336 \times 10^{-11})$	$\mathbf{V}_s = \frac{10^8}{c}\mathbf{V}$ $(10^8 c^{-1} = 3{\cdot}336 \times 10^{-3})$	$\mathbf{V}_s$ electrostatic units

(joule) is the work done by a coulomb of electricity passing through a resistance of 1 ohm. Further discussion of electrical units is provided by Bond *.

With regard to the non-electrical units introduced, the following points may be noted. The calorie is defined as the quantity of heat necessary to raise 1 gram of water from 14·5° C. to 15·5° C. (sometimes called the 15° calorie). It may be observed that the factors provided are practically unaffected, within the limits of accuracy used, if the "normal" calorie (one-hundredth of the heat required to raise 1 gram of water from 0° C. to 100° C.) is employed instead. The large calorie, or Calorie, may be described as a kilogram-calorie (1000 calories = 1 Calorie). Units of wave-length are: Siegbahn unit X (cm. $\times 10^{-11}$), the Ångstrom unit Å.U. (cm. $\times 10^{-8}$), the millimicron $\mu\mu$ (cm. $\times 10^{-7}$), and the micron μ

* Phil. Mag. (7) ix. pp. 842–847 (1930).

(cm. $\times 10^{-4}$). Numbers in other units may be derived from those in Ångstrom units by means of the relations:

Wave-length in Siegbahn units	10^{3}	$\times$ number in Å.U.
millimicrons	10^{-1}	
microns	10^{-4}	

Atomic masses and gram-molecules are expressed on the O = 16 scale. Further information concerned with the units employed may be gained by inspection of equations (1) below.

2. *Values of the Physical Constants.*

The physical constants required for the present purpose are: (1) the electronic charge e; (2) the electronic mass m; (3) the elementary quantum h; (4) the Avogadro (Loschmidt) number N; (5) the heat equivalent of mechanical energy k; (6) the velocity of light *in vacuo* c. The values assigned to the first four named are not independent of each other, and depend ultimately upon the values chosen for the experimental quantities e and e/m. Uncertainty in the value of e may be as much as 0·5 per cent., whilst experiments based on deflexion of cathode rays yield values of the e/m ratio which differ from the spectroscopic estimates by about 0·4 per cent., an amount outside the estimated individual errors in each case. Thus Birge* quotes $e/m = 1{\cdot}769(\pm 0{\cdot}002) \times 10^{8}$ (deflexion), and $e/m = 1{\cdot}761(\pm 0{\cdot}001) \times 10^{8}$ int. coul. per gram (spectroscopic). Millikan's value of e, derived in 1917, and regarded as the best available in 1926 (see the 'International Critical Tables,' i., also Geiger and Scheel's *Handbuch der Physik*, ii., article by Henning and Jaeger, pp. 487–518), was $4{\cdot}774(\pm 0{\cdot}005) \times 10^{-10}$ E.S. units. Wadlund† obtained a value in exact agreement with this by means of absolute X-ray wave-length measurements. Millikan's latest estimate‡ of $e = 4{\cdot}770(\pm 0{\cdot}005) \times 10^{-10}$ E.S. units tends to fall a little lower. On the other hand, Bäcklin§ has obtained the higher value $4{\cdot}793 \times 10^{-10}(\pm 0{\cdot}3$ per cent.) by the X-ray method, and has discussed‖ the errors inherent in Millikan's and Wadlund's in relation to those of his own experiments. On the whole, it would seem that the X-ray method promises to yield a very accurate value of e, although probably the values obtained by it up to the present time cannot be regarded as

* Phys. Rev. Suppl. i. pp. 1–73 (1929).
† Phys. Rev. (2) xxxii. pp. 841–849 (1928).
‡ Phys. Rev. (2) xxxv. pp. 1231–1237, 1433 (1930).
§ 'Dissertation,' Upsala (1928).
‖ 'Nature,' cxxiii. pp. 409–410 (1929).

very exact. Birge * has made a very comprehensive review of the errors in determining physical constants, in an attempt to state the most reliable values. He discards Bäcklin's estimate, and adopts the spectroscopic e/m ratio. Bond † obtains $e = 4{\cdot}780(\pm 0{\cdot}002) \times 10^{-10}$, and uses the deflexion e/m ratio. The selection of the best numbers for the present purpose is influenced by the consideration that the calculated factors involve spectroscopic numbers, such as wave-number and wave-length. It is deemed advisable to adopt Millikan's estimate, in agreement with that of Birge, $e = \mathbf{4{\cdot}770 \times 10^{-10}}$ E.S. unit, in conjunction with the spectroscopic $e/m = 1{\cdot}761 \times 10^{8}$ coul. gr.$^{-1}$, or $1{\cdot}761 \times 10^{8} \times 2{\cdot}998 \times 10^{9} = 5{\cdot}279 \times 10^{17}$ E.S. units gr.$^{-1}$, using Table I. This yields $m = \mathbf{9{\cdot}035 \times 10^{-28}}$ gram. The corresponding numbers $h = \mathbf{6{\cdot}547 \times 10^{-27}}$ erg second and $\mathrm{N} = \mathbf{6{\cdot}064 \times 10^{23}}$ per g-mol. are used, together with $k = \mathbf{2{\cdot}390 \times 10^{-11}}$ kilogram-calorie per erg, and $c = \mathbf{2{\cdot}998 \times 10^{10}}$ cms. per second. The value of e in E.M. units is $1{\cdot}591 \times 10^{-20}$, using the conversion factor $3{\cdot}336 \times 10^{-11}$ of Table I.

3. *Relations between the Constants.*

Since factors which are functions of the six constants named are in question, it may be appropriate to make a brief survey of their interrelations. The mass of the hydrogen atom obtained spectroscopically on the He = 4 scale is 1·00072. If H = 1·008 on the O = 16 basis, the absolute mass is $1{\cdot}008/\mathrm{N} = 1{\cdot}662 \times 10^{-24}$ gram, whence, making allowance for the mass of the electron, that of the proton m_p may be taken as $1{\cdot}661 \times 10^{-24}$ gram. This gives $m_p/m = 1{\cdot}661 \times 10^{-24}/9{\cdot}035 \times 10^{-28} = \mathbf{1838}$. Fürth ‡ has obtained a value in exact agreement with this by calculations based on quantum considerations. The best value of the ratio obtained from deflexion experiments, however, is 1847 ± 2. The suggestion has been made that the difference is a real one, and that actually slightly different quantities are in question. Further experiment is needed to decide this point definitely.

Perles § finds that the m_p/m ratio may be expressed by $hc(\pi - 1)/e^2$. Eddington ‖ advances theoretical reasons for supposing that the "fine structure constant" $hc/2\pi e^2$ should be an integer equal to 137. If both these conclusions may be accepted, Perles' value of the ratio may be expressed as

* *Loc. cit.*
† Phil. Mag. (7) x. pp. 994–1003 (1930).
‡ *Zeit. Physik*, lvii. pp. 429–446 (1929).
§ *Naturwiss.* xvi. pp. 1094–1095 (1928).
‖ Proc. Roy. Soc. A, cxxvi. pp. 696–728 (1930).

a function of π, $m_p/m = 137 \times 2\pi(\pi - 1)$, or 1843·5, which is near the arithmetic mean of the deflexion and spectroscopic values *. Spectroscopic results, however, do not appear to confirm the integral nature of the fine structure constant; the value is about 137·3. The relatively great mass of the proton has not been explained.

Witmer † has pointed out that the square root of 1847 is 42·98, or very nearly 43, which is half the atomic number of niton. Such relationships savour of coincidence, although the possibility of physical meaning cannot be quite ruled out. The question whether certain functions of the fundamental constants are integral or not can hardly be decided with the values at present available.

4. *Explanation of the Conversion Table III.*

Table III. is concerned with ten related magnitudes with respect to any pair amongst them, the interconversion factors involving the six physical constants previously considered. Energy may be expressed directly as J joules, E ergs, or H calories, or indirectly in terms of an electron moving under a P.D. of V volts or with a velocity **v** cm. per sec. Chemists sometimes require the quantity U kilogram-cal. per gr. molecule. Further, the related numbers ν cycles per second, wave-number **w** waves per sec., and wave-length λ Å.U. are widely used in spectroscopy. If λ is now the wave-length in Å.U. of radiant energy of maximum density in a closed space at T° absolute, the relation $\lambda T = 10^8 hcN/\alpha K$ may be used, where α is the solution of $\alpha = 5(1 - e^{-\alpha})$, whence $\alpha = 4{\cdot}9651$, and $K = 8{\cdot}3136 \times 10^7$ ergs per gr. molecule, giving $\lambda T = 2{\cdot}885 \times 10^7$ ‡. Thus T may be obtained from λ (or any other of the related numbers here considered), though temperature is not included in Table III. Last, the relativity theory requires correspondence between energy and mass M grams, so that it becomes useful in certain connexions to calculate the equivalent mass of an energy quantum or photon, or, conversely, in the annihilation theory, to derive the energy corresponding to the disappearance of a given amount of matter. The relations between the ten magnitudes E, J, V, **v**, H, U, **w**, ν, λ, M may be expressed as follows:—

$$E = 10^7 J = \frac{10^8 eV}{c} = \frac{m\mathbf{v}^2}{2} = \frac{H}{10^3 k} = \frac{U}{kN} = ch\mathbf{w} = h\nu = \frac{10^8 ch}{\lambda} = c^2 M \quad . \quad . \quad . \quad . \quad (1)$$

* Clark. *Naturwiss.* xi. p. 182 (1932).
† 'Nature,' cxxiv. pp. 180–181 (1929).
‡ Donnan, 'Nature,' cxxviii. pp. 290–292 (1931).

Table III. is constructed using these relationships together with the values of the constants with the accuracy obtainable with ordinary four-figure logarithms, and shows in each compartment: (1) the relation between two magnitudes in the form $X = aY$; (2) the value of $\log_{10}(aY)$; (3) the expression aY with the appropriate value of the factor a. The compartments are numbered 1 to 90. A few examples of the use of the table follow in the form of problem and solution. Others might be cited, as in the calculation of lattice energies, electron affinities, and so on.

1. *Express* 50 *joules in calories and in equivalent electron volts.* Using compartments 37 and 10 of Table III., 50 joules $= 0{\cdot}239 \times 50 = \mathbf{11{\cdot}95}$ calories $= 6{\cdot}287 \times 10^{18} \times 50 = \mathbf{3{\cdot}144 \times 10^{20}}$ electron volts.

2. *Calculate the electronic velocity and quantum frequency necessary to ionize the hydrogen atom, the ionization potential being* 13·57 *volts.* By factors of compartments 20 and 56: 13·57 volts $= 5{\cdot}934 \times 10^7 \times 13{\cdot}57^{\frac{1}{2}} = \mathbf{2{\cdot}186 \times 10^8}$ cms. per sec. $= 2{\cdot}430 \times 10^{14} \times 13{\cdot}57 = \mathbf{3{\cdot}298 \times 10^{15}}$ cycles per second. The corresponding wave-length is found to be **914 Å.U.**

3. *Find the energy limits of the visible spectrum from* 4000 Å.U. *to* 8000 Å.U. *in equivalent electron volts.* Using compartment 17 of the table, 4000 Å.U. $= 1{\cdot}234 \times 10^4/4000 = \mathbf{3{\cdot}085}$ electron volts; similarly, 8000 Å.U. $= \mathbf{1{\cdot}543}$ electron volts. Separations of this order of magnitude appear in the lower vibrational and rotational levels of molecules, so that such levels are likely to be of importance in determining shifts in the Raman effect, as is found to be the case.

4. *What is the heat of dissociation of* H_2 *at the absorption limit in the Schumann region of* 850 Å.U. *in electron volts and Cal. per gr. molecule?* Applying factors in compartments 17 and 47, 850 Å.U. $= 1{\cdot}234 \times 10^4/850 = \mathbf{14{\cdot}52}$ electron volts $= 23{\cdot}05 \times 14{\cdot}52 = \mathbf{334{\cdot}7}$ Calories per gr. molecule. Dissociation occurs into one normal and one excited H atom (Dieke and Hopfield, Witmer); the heat of dissociation includes the energy of excitation of the hydrogen atom (10·15 equivalent electron volts).

5. *Calculate the wave-length of radiation equivalent to the annihilation of a proton by an electron.* By the appropriate factor in compartment 81, it is required to convert the mass $1{\cdot}662 \times 10^{-24}$ gram, giving $1{\cdot}662 \times 10^{-24}$ gram $= 2{\cdot}184 \times 10^{-29}/1{\cdot}662 \times 10^{-24} = \mathbf{1{\cdot}313 \times 10^{-5}}$ Å.U.

Department of Inorganic Chemistry,
The University of Leeds.
January 4th, 1932.

XXXI. *Periodic Orbits in a Field of Force defined by a certain Potential.* By M. A. Higab, *M.Sc., Ph.D., Lecturer in Mathematics in the Egyptian University, Cairo**.

IN a previous paper the condition for the existence of periodic orbits, when a particle of unit mass moves in a space of two dimensions in a field of force whose potential is

$$V=\mu\int F(r)\,dr+\frac{\lambda}{r^2}\int f(\theta)\,d\theta,$$

where r and θ are the usual polar coordinates, λ and μ are constants, is found.

The aim of the present paper is to establish these conditions if the particle moves in a space of three dimensions.

The equations of motion are:

$$\ddot{r}-r\dot{\theta}^2-r\sin^2\theta.\dot{\phi}^2=-\mu F(r)+\frac{2\lambda}{r^3}W(\theta), \quad (1)$$

$$\frac{1}{r}\frac{d}{dt}(r^2\dot{\theta})-r\sin\theta\cos\theta.\dot{\phi}^2=-\frac{\lambda f(\theta)}{r^3}, \quad . \quad . \quad . \quad . \quad (2)$$

$$r^2\sin^2\theta.\dot{\phi}=h, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where r, θ, ϕ are the usual polar coordinates in three dimensions, and h is constant and

$$W(\theta)=\int f(\theta)\,d\theta.$$

There are three types of motion which are to be considered separately :—

I. Motion on a right circular cone defined by $\theta=$constant.

II. Motion on a sphere defined by $r=$constant.

III. General motion, where all the coordinates vary.

I. Motion on a Right Circular Cone.

Putting $\theta=\alpha$ (where α is constant) in the equations (1), (2), (3), we get the equations of motion to be

$$\ddot{r}-r\sin^2\alpha.\dot{\phi}^2=-\mu F(r)+\frac{2\lambda}{r^3}W(\alpha), \quad . \quad . \quad (1)$$

$$r^4\dot{\phi}^2=\lambda f(\alpha)\sec\alpha\operatorname{cosec}\alpha, \quad . \quad . \quad . \quad (2)$$

$$r^4\dot{\phi}^2=h^2\operatorname{cosec}^4\alpha. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

* Communicated by the Author.

The equations (2) and (3) are identical if

$$h^2 = \lambda f(\alpha) \sin^3 \alpha \sec \alpha. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Since h^2 is positive, we must have

$$\lambda f(\alpha) \sin^3 \alpha \sec \alpha,$$

to be always positive. This condition defines the semi-vertical angle of the right circular cone on which the motion is to take place.

Eliminating $\dot{\phi}$ between (1) and (2) we get

$$\ddot{r} = -\mu F(r) + \frac{A}{r^3}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where

$$A = \lambda[2W(\alpha) + \tan \alpha f(\alpha)].$$

The integral of (5) is

$$\dot{r}^2 = -2\mu \int F(r)\, dr - \frac{A}{r^2} + B, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where B is constant and equals twice the total energy of the system.

The Differential Equation of the Path.

From equations (2) and (6) we get

$$\frac{1}{r^4}\left(\frac{dr}{d\phi}\right)^2 = \frac{B - \frac{A}{r^2} - 2\mu \int F(r)\, dr}{\lambda f(\alpha) \sec \alpha \operatorname{cosec} \alpha}. \quad . \quad . \quad (7)$$

Putting $u = \frac{1}{r}$ and writing $\frac{du}{d\phi} = u_1$, we get (7) to be

$$u_1^2 = \frac{B - A u^2 + 2\mu \phi(u)}{\lambda f(\alpha) \sec \alpha \operatorname{cosec} \alpha},$$

where

$$\phi(u) = \int F\left(\frac{1}{u}\right) \frac{du}{u^2}.$$

Periodic Orbits.

A necessary condition for the existence of periodic orbits is that u must be oscillatory. Putting $u_1 = 0$, we get

$$B - Au^2 + 2\mu \phi(u) = 0. \quad . \quad . \quad . \quad . \quad (8)$$

Let α_1 and α_2 be two positive roots of equation (8) where $\alpha_1 > \alpha_2$;

$$\therefore \qquad A = 2\mu \frac{\phi(\alpha_1) - \phi(\alpha_2)}{\alpha_1^2 - \alpha_2^2}$$

and

$$B = 2\mu \frac{\alpha_2^2 \phi(\alpha_1) - \alpha_1^2 \phi(\alpha_2)}{\alpha_1^2 - \alpha_2^2}.$$

In this case u oscillates between the maximum and minimum values α_1 and α_2 respectively.

The equation of the path can be put in the form

$$\int_{u_0}^{u} \frac{du}{\sqrt{2\mu \frac{\alpha_2^2 \phi(\alpha_1) - \alpha_1^2 \phi(\alpha_2)}{\alpha_1^2 - \alpha_2^2} - 2\mu \frac{\phi(\alpha_1) - \phi(\alpha_2)}{\alpha_1^2 - \alpha_2^2} u^2 + 2\mu\phi(u)}} = \left(\frac{\sin\alpha\cos\alpha}{\lambda f(\alpha)}\right)^{\frac{1}{2}} (\phi - \phi_0),$$

i. e.,

$$\frac{1}{\sqrt{c}} [\Phi(u) - \Phi(u_0)] = \left(\frac{\sin\alpha\cos\alpha}{\lambda f(\alpha)}\right)^{\frac{1}{2}} (\phi - \phi_0),$$

where u_0 and ϕ_0 are the initial values of u and ϕ respectively, and c is constant depending upon the coefficients of the quantity

$$2\mu \frac{\alpha_2^2 \phi(\alpha_1) - \alpha_1^2 \phi(\alpha_2)}{\alpha_1^2 - \alpha_2^2} - 2\mu \frac{\phi(\alpha_1) - \phi(\alpha_2)}{\alpha_1^2 - \alpha_2^2} u^2 + 2\mu\phi(u),$$

that arises during the process of integration.

The remaining conditions for the existence of periodic orbits are

$$\frac{c \sin\alpha\cos\alpha}{\lambda f(\alpha)} = \frac{n^2}{k^2},$$

and $\Phi(u)$ must be an inverse function obeying the law

$$\Phi^{-1}\Phi(u) = \Phi^{-1}[\Phi(u) + 2n\pi] = u,$$

where k and n are any positive integers.

If these conditions are satisfied, we must have

$$\Phi(u) = \Phi(u_0) + 2n\pi ;$$

$$\therefore \quad \Phi^{-1}\Phi(u) = \Phi^{-1}[\Phi(u_0) + 2n\pi] = \Phi^{-1}\Phi(u),$$

i. e., $\qquad u = u_0 ;$

i. e., u returns to its original value and periodic orbits are formed.

II. Motion on a Sphere.

From the equations (1), (2), (3), p. 298, if we put $r=a$, where a is constant, we can derive the following equations:

$$a^4\dot{\theta}^2=\mu a^3 \mathrm{F}(a)-2\lambda \mathrm{W}(\theta)-\frac{h^2}{\sin^2\theta}, \quad . \quad (1)$$

$$a^4\dot{\theta}^2=\mathrm{A}-2\lambda \mathrm{W}(\theta)-\frac{h^2}{\sin^2\theta}, \quad . \quad . \quad . \quad . \quad (2)$$

$$a^2\sin^2\theta.\dot{\phi}=h. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The equations (1) and (2) are identical if $\mathrm{A}=\mu a^3 \mathrm{F}(a)$. Thus the equations of motion on the surface of a sphere give rise to the following two equations:

$$a^4\dot{\theta}^2=\mu a^3 \mathrm{F}(a)-2\lambda \mathrm{W}(\theta)-\frac{h^2}{\sin^2\theta},$$

$$a^2\sin^2\theta.\dot{\phi}=h.$$

Now for a real motion to exist θ must oscillate between the two real values α and β, where α and β are two roots of the equation

$$\mu a^3 \mathrm{F}(a)-2\lambda \mathrm{W}(\theta)-\frac{h^2}{\sin^2\theta}=0.$$

The differential equation of the path is

$$\left(\frac{d\theta}{d\phi}\right)^2=\frac{\left[\mu a^3 \mathrm{F}(a)-2\lambda \mathrm{W}(\theta)-\frac{h^2}{\sin^2\theta}\right]\sin^4\theta}{h^2}. \quad (4)$$

In equation (4) put

$$\cos\theta=\cos\alpha\cos^2\chi+\cos\beta\sin^2\chi,$$

the differential equation of the path takes the form

$$\mathrm{H}\frac{d\chi}{\Phi(\chi)}=d\phi,$$

where H is constant.

The equation of the path is therefore

$$\mathrm{H}\int_{\chi_0}^{\chi}\frac{d\chi}{\Phi(\chi)}=\phi-\phi_0,$$

where χ_0 is the value of χ corresponding to $\theta=\theta_0$, and ϕ_0 is the initial value of ϕ.

Periodic Orbits.

The condition for periodic orbits is

$$H\int_{\chi_0}^{2k\pi+\chi_0}\frac{d\chi}{\Phi(\chi)}=2n\pi,$$

where n is a positive integer.

If this condition is satisfied, then ϕ returns to its original value and periodic orbits are formed.

III. General Motion.

From the equations (1), (2), (3), p. 298, we can derive the following equations:

$$\dot{r}^2=B-\frac{A}{r^2}-2\mu\int F(r)\,dr, \quad . \quad . \quad . \quad (1)$$

$$r^4\dot{\theta}^2=A-2\lambda W(\theta)-\frac{h^2}{\sin^2\theta}, \quad . \quad . \quad . \quad (2)$$

$$r^2\sin^2\theta.\dot{\phi}=h. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The differential equations of the path are:

$$\left(\frac{du}{d\theta}\right)^2=\frac{B-Au^2+2\mu\phi(u)}{A-2\lambda W(\theta)-\frac{h^2}{\sin^2\theta}} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and

$$\left(\frac{d\phi}{d\theta}\right)^2=\frac{h^2}{\sin^4\theta\left[A-2\lambda W(\theta)-\frac{h^2}{\sin^2\theta}\right]}. \quad . \quad (5)$$

For a real motion to exist θ must oscillate between the two real values θ_1 and θ_2, where θ_1 and θ_2 are two roots of the equation

$$A-2\lambda W(\theta)-\frac{h^2}{\sin^2\theta}=0.$$

In the equations (4) and (5) put

$$\cos\theta=\cos\theta_1\cos^2\chi+\cos\theta_2\sin^2\chi.$$

In this case the differential equations of the path take the form

$$\frac{du}{\sqrt{B-Au^2+2\mu\phi(u)}}=\frac{H_1d\chi}{F_1(\chi)}$$

and

$$d\phi=\frac{H_2d\chi}{F_2(\chi)},$$

where

$$u = \frac{1}{r}, \qquad \phi(u) = \int \mathrm{F}\left(\frac{1}{u}\right) \frac{du}{u^2},$$

H_1 and H_2 are constants.

Periodic Orbits.

A necessary condition for the existence of periodic orbits is that u must be oscillatory. Putting $\frac{du}{d\theta} = 0$, we get

$$\mathrm{B} - \mathrm{A}u^2 + 2\mu\,\phi(u) = 0. \quad . \quad . \quad . \quad . \quad (6)$$

Let α_1 and α_2 be two positive real roots of the equation (6), where $\alpha_1 > \alpha_2$;

$$\therefore \qquad \mathrm{A} = 2\mu \frac{\phi(\alpha_1) - \phi(\alpha_2)}{\alpha_1^2 - \alpha_2^2}$$

and

$$\mathrm{B} = 2\mu \frac{\alpha_2^2\,\phi(\alpha_1) - \alpha_1^2\,\phi(\alpha_2)}{\alpha_1^2 - \alpha_2^2}.$$

In this case u oscillates between the maximum and minimum values α_1 and α_2 respectively.

The equations of the path can be put in the form

$$\Phi(u) - \Phi(u_0) = \mathrm{H}_1' \int_{\chi_0}^{\chi} \frac{d\chi}{\mathrm{F}_1(\chi)}$$

and

$$\phi - \phi_0 = \mathrm{H}_2 \int_{\chi_0}^{\chi} \frac{d\chi}{\mathrm{F}_2(\chi)},$$

where u_0, ϕ_0, χ_0 are the initial values of u, ϕ, and χ respectively, and H_1' is constant.

The remaining conditions for periodic orbits are

(i.) $\mathrm{H}_1' \int_{\chi_0}^{2k\pi+\chi_0} \frac{d\chi}{\mathrm{F}_1(\chi)} = 2m\pi,$

(ii.) $\mathrm{H} \int_{\chi_0}^{2k\pi+\chi_0} \frac{d\chi}{\mathrm{F}_2(\chi)} = 2n\pi,$

(iii.) $\Phi(u)$ must be an inverse function obeying the law,

$$\Phi^{-1}\,\Phi(u) = \Phi^{-1}[\Phi(u) + 2m\pi] = u,$$

where k, m, n are positive integers.

If these conditions are satisfied then u returns to its original value u_0, and ϕ returns to its original value ϕ_0, *i. e.*, periodic orbits are formed.

As an application to this paper I refer the reader to a paper by the same author (Phil. Mag. vii. pp. 31–52, January 1929).

Summary.

The conditions for the existence of periodic orbits, when a particle of unit mass moves in a field of force whose potential is

$$V=\mu\int F(r)\,dr+\frac{\lambda}{r^2}\int f(\theta)\,d\theta,$$

is found.

XXXII. *Three Dimensional Periodic Orbits in the Field of a Non-Neutral Atom.* *By* M. A. El-Sherbini, *B.Sc.(Egypt), The Faculty of Science, The Egyptian University* *.

I. *Introductory.*

THE problem of the three-dimensional motion of a particle in the field of a doublet was dealt with by J. J. Thomson †, who investigated the case of steady motion. J. H. Jeans ‡ integrated the equations of motion and obtained some results of interest. The corresponding problem in two dimensions was discussed by D. Wrinch §, who obtained conditions for the existence of semi-circular periodic orbits. M. A. Higab ‖ generalized the problem to include the presence of a central inverse-squared field, already dealt with by G. Greenhill ¶ as a two-dimensional problem. Higab obtained the conditions for periodicity both in the two-dimensional and in the three-dimensional cases. Leigh Page **, by considering the case of a relatively weak doublet, was able to obtain the approximate equations of the path.

The object of the present paper is to establish, in the general case, the existence of an infinite number of periodic orbits in the field of a relatively weak doublet.

* Communicated by Dr. M. A. Higab, M.Sc.
† Phil. Mag. p. 244 (1910).
‡ *Ibid.* p. 380 (1910).
§ *Ibid.* p. 993 (1913).
‖ *Ibid.* p. 783 (1929).
¶ *Ibid.* p. 372 (1913).
** *Ibid.* p. 314 (1930).

II. *Equations of Motion.*

The equations of motion are

$$\ddot{r}-r\dot{\theta}^2-r\sin^2\theta.\dot{\phi}^2=-\frac{\mu}{r^2}-\frac{2\lambda\cos\theta}{r^3}, \quad . \quad (1)$$

$$\frac{1}{r}\frac{d}{dt}(r^2\dot{\theta})-r\sin\theta\cos\theta.\dot{\phi}^2=-\frac{\lambda\sin\theta}{r^3}, \quad . \quad . \quad . \quad (2)$$

$$\frac{1}{r\sin\theta}\frac{d}{dt}(r^2\sin^2\theta.\dot{\phi})=0, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where r, θ, ϕ are the usual polar coordinates, λ the strength of the doublet and μ the constant of central force (both μ and λ are positive), we get from (3)

$$r^2\sin^2\theta.\dot{\phi}=h, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Also we can derive from (1), (2), and (4),

$$\dot{r}^2=-2w+\frac{2\mu}{r}-\frac{a^2}{r^2}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$r^4\dot{\theta}^2=a^2+2\lambda\cos\theta-\frac{h^2}{\sin^2\theta}. \quad . \quad . \quad . \quad . \quad (6)$$

The constants* μ, λ, h, a, and w have the following physical dimensions:

$$\mu=\frac{L^3}{T^2}, \qquad \lambda=\frac{L^4}{T^2}, \qquad a=h=\frac{L^2}{T}, \qquad w=\frac{L^2}{T^2}. \quad (7)$$

The motion† is included between two cones of semi-vertical angles α, β, where $\cos\alpha$, $\cos\beta$, and $-\cosh\gamma$ are the roots of the cubic

$$a^2+2\lambda\cos\theta-\frac{h^2}{\sin^2\theta}=0. \quad . \quad . \quad . \quad . \quad (8)$$

Let

$$\cos\theta=x, \quad \cos\alpha=x_2, \quad \cos\beta=x_1 \quad -\cosh\gamma=x_0 \text{ and } u=\frac{1}{r}. \quad . \quad . \quad . \quad (9)$$

The differential equations of the path become

$$2\lambda(x_2-x)(x-x_1)(x-x_0)\left(\frac{du}{dx}\right)^2=2\mu u-a^2u^2+w \quad (10)$$

* See Page's paper quoted above.
† See Higab's paper quoted above.

and

$$\left(\frac{d\phi}{dx}\right)^2 = \frac{h^2}{2\lambda(1-x^2)^2(x_2-x)(x-x_1)(x-x_0)}, \qquad (11)$$

a^2 and w must be positive *.

In the differential equations of the path put

$$x = x_2\cos^2\chi + x_1\sin^2\chi. \quad . \quad . \quad . \quad . \quad (12)$$

We then have as the equations of the path :

$$\frac{l}{r} = 1 + e\cos\left[c + \left\{\frac{2a^2}{\lambda(x_2-x_0)}\right\}^{\frac{1}{2}}\int\frac{d\chi}{\left(1-\frac{x_2-x_1}{x_2-x_0}\sin^2\chi\right)^{\frac{1}{2}}}\right]$$

and . . . (13)

$$\phi-\phi_0\frac{h}{\{2\lambda(x_2-x_0)\}}$$

$$\times\left[\frac{1}{1+x_2}\int_0^{\chi}\frac{d\chi}{\left(1-\frac{x_2-x_1}{1+x_2}\sin^2\chi\right)\left(1-\frac{x_2-x_1}{x_2-x_0}\sin^2\chi\right)^{\frac{1}{2}}}\right.$$

$$+\frac{1}{1-x_2}\int_0^{\chi}\frac{d\chi}{\left(1+\frac{x_2-x_1}{1-x_2}\sin^2\chi\right)\left(1-\frac{x_2-x_1}{x_2-x_0}\sin^2\chi\right)^{\frac{1}{2}}}$$

$$-\frac{1}{1+x_2}\int_0^{\chi_0}\frac{d\chi}{\left(1-\frac{x_2-x_1}{1+x_2}\sin^2\chi\right)\left(1-\frac{x_2-x_1}{x_2-x_0}\sin^2\chi\right)^{\frac{1}{2}}}$$

$$\left.-\frac{1}{1-x_2}\int_0^{\chi_0}\frac{d\chi}{\left(1+\frac{x_2-x_1}{1-x_2}\sin^2\chi\right)\left(1-\frac{x_2-x_1}{x_2-x_0}\sin^2\chi\right)^{\frac{1}{2}}}\right],$$

. . . (14)

where

$$\left.\begin{aligned}&\frac{e^2}{l^2} = \frac{w}{a^2} + \frac{\mu^2}{a^4}, \qquad \frac{\mu}{a^2} = \frac{1}{l}, \qquad c = \text{constant},\\ &\phi_0 \text{ and } \chi_0 \text{ are the initial values of } \phi \text{ and } \chi \text{ respectively}\end{aligned}\right\}. \quad . \quad . \quad . \quad (15)$$

III. *Periodic Orbits.*

The conditions for the existence of periodic orbits are :

(i.) $e<1$. (This makes r oscillatory.) . . . . . (16)

* See Page's paper quoted above.

(ii.) $$\frac{(1-x_2^2-x_1^2-x_1x_2)^{\frac{1}{2}}}{(1+2x_1x_2+x_2^2)^{\frac{1}{2}}} \int_0^{k\pi} \frac{d\chi}{\left(1-\frac{x_2^2-x_1^2}{1+2x_1x_2+x_2^2}\sin^2\chi\right)^{\frac{1}{2}}} = m\pi, \quad . \quad . \quad (17)$$

(iii.) $$\frac{(1-x_2^2)^{\frac{1}{2}}(1-x_1^2)^{\frac{1}{2}}}{(1+2x_1x_2+x_2^2)^{\frac{1}{2}}} \left[\frac{1}{1+x_2}\int_0^{k\pi} \frac{d\chi}{\left(1-\frac{x_2-x_1}{1-x_2}\sin^2\chi\right)\left(1-\frac{x_2^2-x_1^2}{1+2x_1x_2+x_2^2}\sin^2\chi\right)^{\frac{1}{2}}}\right.$$

$$\left. + \frac{1}{1-x_2}\int_0^{k\pi} \frac{d\chi}{\left(1+\frac{x_2-x_1}{1-x_2}\sin^2\chi\right)\left(1-\frac{x_2^2-x_1^2}{1+2x_1x_2+x_2^2}\sin^2\chi\right)^{\frac{1}{2}}}\right] = 2m\pi. \quad . \quad . \quad . \quad . \quad (18)$$

In equation (8) let λ be small, the approximate value of the roots are

$$x_0 = -\frac{a^2}{2\lambda}\left\{1+\frac{4h^2\lambda^2}{a^6}+\ldots\right\}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

$$x_1 = -\left(1-\frac{h^2}{a^2}\right)^{\frac{1}{2}} + \frac{\lambda h^2}{a^4} + \frac{2\lambda^2h^2\left(1-\frac{5}{4}\frac{h^2}{a^2}\right)}{a^6\left(1-\frac{h^2}{a^2}\right)^{\frac{1}{2}}} + \ldots, \quad (20)$$

$$x_2 = \left(1-\frac{h^2}{a^2}\right)^{\frac{1}{2}} + \frac{\lambda h^2}{a^4} - \frac{2\lambda^2h^2\left(1-\frac{5}{4}\frac{h^2}{a^2}\right)}{a^6\left(1-\frac{h^2}{a^2}\right)^{\frac{1}{2}}} + \ldots. \quad (21)$$

Substituting in (17) and (18) and applying the following formulæ, with

$$a=1 \quad \text{and} \quad |b| = \left|\sqrt{1-\frac{h^2}{a^2}}\right| < 1:$$

$$\int_0^{k\pi} \frac{d\chi}{(a+b\cos\chi)^n} = \frac{(-1)^{n-1}}{(n-1)!}k\pi\frac{\partial^{n-1}}{\partial a^{n-1}}\frac{1}{(a^2-b^2)^{\frac{1}{2}}}, \quad (22)$$

$$\int_0^{k\pi} \frac{d\chi}{(a+b\cos\chi)^n} = \frac{(-1)^{n-1}}{(n-1)!}k\pi\frac{\partial^{n-1}}{\partial b^{n-1}}\frac{1}{(a^2-b^2)^{\frac{1}{2}}}. \quad (23)$$

We get as the conditions for the existence of periodic orbits,

(i.) $e<1$, ... (24)

$$\text{(ii.)}\quad m=k\left[1+\frac{3}{4}\frac{\lambda^2}{a^4}\left(1-\frac{2h^2}{a^2}\right)\right], \quad . \quad . \quad (25)$$

$$\text{(iii.)}\quad n=k\left[1-\frac{3}{2}\frac{\lambda^2}{a^4}\left(\frac{h}{a}\right)\right]. \quad . \quad . \quad . \quad . \quad (26)$$

IV. *General Motion.*

In the last two equations k is a definite quantity which determines the order of the orbit ; for instance, orbits of order one are given by $k=1$, orbits of order two are given by $k=2$, ... etc.

These two equations (25) and (26) can be interpreted as determining a^2 and h^2 for given values of λ, m, n, and k.

Equation (25) can be put in the form

$$h^2=\frac{a^2}{2}+\frac{2}{3}\frac{a^6}{\lambda^2}\left(1-\frac{m}{k}\right). \quad . \quad . \quad . \quad (27a)$$

Using this relation in (26) we get,

$$a^2=\pm\frac{\sqrt{6}\,\lambda}{2\left(1-\frac{n}{k}\right)}\left(1-\frac{m}{k}\right)^{\frac{1}{2}}. \quad . \quad . \quad . \quad (28a)$$

For the existence of periodic orbits a^2 and h^2 must both be positive, which conditions can be satisfied if

$$m<k \quad \text{and} \quad n><k. \quad . \quad . \quad . \quad . \quad (29a)$$

The positive value $\frac{h}{a^2}$ is subject to the condition that it must be less than unity ; therefore, we must have

$$0<\tfrac{1}{2}+\frac{(k-m)^2}{(k-n)^2}<1. \quad . \quad . \quad . \quad . \quad (30)$$

Also periodic orbits exist when

$$m=k \quad \text{and} \quad n><k. \quad . \quad . \quad . \quad . \quad (29b)$$

For, if $m=k$, then the condition (25) reduces to

$$h^2=\frac{a^2}{2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27b)$$

Substituting in (26) we get

$$a^4=\pm\frac{3\sqrt{2}}{4}\frac{\lambda^2}{\left(1-\frac{n}{k}\right)}. \quad . \quad . \quad . \quad . \quad . \quad (28b)$$

On the other hand if $n=k$, the motion is in the azimuthal plane and the condition for periodic orbits becomes the same as that in the two-dimensional case, if we approximate the latter supposing λ small.

For the condition of periodicity in the two-dimensional case* is

$$\int_0^{k\pi} \frac{d\chi}{\left(1-\frac{4\lambda}{a^2+2\lambda}\sin^2\chi\right)^{\frac{1}{2}}} = \frac{m\pi}{\left(1-\frac{2\lambda}{a^2+2\lambda}\right)^{\frac{1}{2}}}, \quad . \quad (31)$$

which leads to the approximate condition

$$m=k\left[1+\frac{3}{4}\frac{\lambda^2}{a^4}\right], \quad . \quad . \quad . \quad . \quad . \quad (32)$$

and this is the same as equation (25) if we put $h=0$.

The following is a scheme for the possible values of m and n for the existence of periodic orbits of first, second, and third order.

k.	m.	n.
1	1	2, 3, 4, 5, 6, ... etc.
2	1	4, 5, 6, 7, 8, ... etc.
	2	1 ; 3, 4, 5, 6, ... etc.
3	1	6, 7, 8, 9, 10, ... etc.
	2	1 ; 5, 6, 7, 8, ... etc
	3	1, 2 ; 4, 5, 6, ... etc.

We see that there exists ∞^3 of periodic orbits in this case.

V. *Motion on the Surface of a Sphere.*

The condition for the existence of periodic orbits is (26) ; thus for given values of a, n, and k, this equation can be interpreted as determining h. It is easy to see that ∞^2 of periodic orbits exist in this case.

The motion in this case is always included between two cones of semi-vertical angle α and β, as indicated before. Since $\dot{\phi}$ does not change sign, or even vanish, as is easily seen from equation (4), it follows that there are no loops or cusps. Also the path touches the two co-latitudes $\theta=\alpha$ and $\theta=\beta$ horizontally.

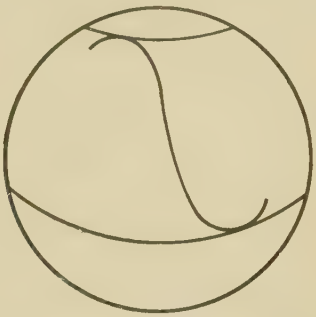
The general form of the curve is as shown in the annexed figure.

Summary.

The three-dimensional motion of a particle in the field of a non-neutral atom is considered. The conditions for the

* Phil. Mag. p. 786 (1929), two dimensional periodic orbits by Higab.

existence of periodic orbits are found for a relatively weak doublet-strength. It is shown that these conditions can be satisfied and that an infinite number of periodic orbits exist.



My thanks are due to Dr. M. A. Higab, under whose direction the above work was done.

XXXIII. *The Theory of Electrolytic Polarization.* *By* Hugo Fricke, *The Walter B. James Laboratory for Biophysics, The Biological Laboratory, Cold Spring Harbour, L.I., New York* *.

Synopsis.

C_p designates the polarization capacity, R_p the polarization resistance, and ψ the phase angle defined by $\tan\psi = C_p\omega R_p$ (ω: angular frequency of alternating current). $V(x)dq$ represents the value of the counter-electromotive force x seconds after a quantity dq of electricity has passed through the electrolytic cell. The following equations are derived:

$$R_p = \int_0^\infty V(x)\cos(\omega x)dx, \quad \ldots\ldots (1)$$

$$1/C_p\omega = \int_0^\infty V(x)\sin(\omega x)dx, \quad \ldots\ldots (2)$$

$$V(x) = \frac{2}{\pi}\int_0^\infty R_p\cos(\omega x)d\omega$$

$$= \frac{2}{\pi}\int_0^\infty (1/C_p\omega)\sin(\omega x)d\omega. \quad (3)\ \&\ (4)$$

* Communicated by the Author.

For $V(x) = \text{const.}_1 . x^{-m}$:

$$C_p = \text{const.}_2 . \omega^{-m}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\psi = m . \pi/2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Thus, when C_p varies inversely as the mth power of the frequency, the phase angle ψ is constant and its value stated by equation (6).

For many electrodes, C_p varies inversely as a power of the frequency, at all frequencies, or over an extended frequency range. For such electrodes equation (6) is found to represent the experimental findings with satisfactory accuracy. Relationships derived from the theories of Warburg and Krüger are represented by equation (6) as special cases. Surveying existing experimental data, it is found that equation (6) generally holds quite closely even when m is not independent of the frequency.

Introduction.

IT is well known that the polarization produced when an alternating current of small density is passed between a metal electrode and an aqueous solution is equivalent to a capacity, the polarization capacity, and a resistance, the polarization resistance, placed in series between the metal and the solution. In the following we shall designate the polarization capacity C_p, the polarization resistance R_p, and the phase angle ψ, defined by $\tan \psi = C_p R_p \omega$, ω being the angular frequency. C_p and R_p depend on the metal, the solution, the frequency, and on the temperature. In this note the frequency dependence only is dealt with.

C_p decreases with increasing frequency, or is, in special cases, independent of the frequency. The relationship is conveniently expressed by $C_p \sim \omega^{-m}$. For certain electrodes m is independent of the frequency, but generally m is dependent on the frequency.

The change of the polarization capacity with the frequency may be considered as caused by a spontaneous depolarization of the electrode. The depolarization is also responsible for the phase shift ψ. Accordingly, we should expect a relationship to exist between the rate at which the polarization capacity changes with the frequency for which m is a measure and the value of ψ. The larger m, the larger ψ. A survey of the experimental material bears out this expectation. We shall in this note discuss this relationship theoretically and examine the existing experimental data from the point of view of the theory.

Our knowledge of the polarization produced by alternating currents at metallic electrodes is in a rather unsatisfactory state, experimentally as well as theoretically.

The polarization produced at reversible electrodes may in some cases be accounted for by a theory worked out by Warburg[1], according to which the polarization capacity changes inversely as the square root of the frequency and the phase angle ψ is constant, equal to 45°. For instance, this is true for mercury in a saturated solution of mercurous sulphate in sulphuric acid, according to Neumann[2]. To explain observations on mercury in solutions of complex mercury salts, Krüger[3] worked out a theory based on the idea that the mercury salt requires an appreciable time for its dissociation. When this time is long compared with the duration of one cycle of the alternating current, this theory leads to the result that the polarization capacity varies inversely as the frequency, while the phase angle ψ is constant, equal to 90°.

A number of experimental studies have been made of irreversible electrodes. However, few have been made over so large a frequency range that a clear idea can be obtained of the variation of the polarization capacity and of the phase angle with the frequency.

Some of the best work is a series of investigations carried out at Cornell University by Merritt[4], Jolliffe[5], Wolff[6], Pierce[7], and Zimmerman[8]. Curves representing the polarization capacity and the phase angle at different frequencies, ranging from a few hundred to a few million cycles per second, have been determined for gold and platinum in diluted sulphuric acid of various strengths. While the curves for different electrodes are not identical, they nevertheless have certain characteristics in common. Over an extended range of frequencies, from a few hundred to about 50,000 cycles/second, the polarization capacity varies inversely as a power of the frequency. m is somewhat different for different electrodes, having an average value of about ·25. Over this range of frequencies, the phase angle ψ is constant. At higher frequencies m increases, reaching in certain cases a constant value of 1/2, in others apparently increasing still higher. ψ increases at the same time. At lower frequencies, m decreases[7], the polarization being, perhaps, at sufficiently low frequencies, or when direct current is used, represented by a pure static capacity.

Besides the Cornell investigations, there is found in the literature a number of investigations of different irreversible electrodes, all made, however, at comparatively low fre-

quencies and over narrow ranges of frequencies. The results differ greatly for different electrodes and even for the same electrode measured by different investigators. In some cases, m is found to be independent of the frequency, in others it is not. ψ is usually remarkably constant. The values of m and ψ vary for different electrodes, from both being near zero to values near 1 for m and 90° for ψ. The experimental uncertainty is, however, considerable, and renewed work may produce more uniform results.

The polarization observed at electrodes which maintain definite electrode potentials is not always of the type described by Warburg's theory, but is more often of the type observed at irreversible electrodes, the reason being, perhaps, that the mechanism regulating the electrode potential works too slowly to be effective during the duration of one cycle of the alternating current.

Theory.

Assume that an alternating current represented by $i = i_0 \cos(\omega t)$ is passed through an electrolytic cell and that the passage of the quantity of electricity idt, at the time t, produces a counter-electromotive force, which at the time T has the value $V(T-t)$. Since experience shows that the principle of superposition holds, the total counter-electromotive force has at the time T the value

$$E = \int_{-\infty}^{T} V(T-t) . i_0 \cos(\omega t) dt.$$

With $t = T-x$ and $dt = -dx$, we obtain

$$E = i_0 \int_0^{\infty} V(x) \cos \omega(T-x) dx$$

$$= i_0 \cos(\omega T) \int_0^{\infty} V(x) \cos(\omega x) dx + i_0 \sin(\omega T) \int_0^{\infty} V(x) \sin(\omega x) dx.$$

We have also

$$E = R_p i_0 \cos(\omega T) + \frac{i_0}{C_p \omega} \sin(\omega T),$$

and, consequently

$$R_p = \int_0^{\infty} V(x) \cos(\omega x) dx, \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{1}{C_p \omega} = \int V(x) \sin(\omega x) dx. \quad . \quad . \quad . \quad . \quad (2)$$

According to a well-known formula [9],

$$V(x) = \frac{2}{\pi}\int_0^\infty R_p \cos(\omega x)d\omega = \frac{2}{\pi}\int_0^\infty \frac{1}{C_p\omega}\sin(\omega x)d\omega. \quad (3)\&(4)$$

By these equations we can calculate $V(x)$ when the complete frequency curve for the polarization capacity or for the polarization resistance has been determined experimentally.

We shall consider here only the case where $V(x)$ is some power of x, which case is of particular interest, since, as pointed out above, it is found for many electrodes that the polarization capacity and the polarization resistance vary as a power of the frequency over the complete, or over an extended, frequency range.

Assume, consequently, that $V(x) = V_0 . x^{-m}[1 \geq m \geq 0]$, and we derive

$$\left.\begin{aligned} R_p = V_0\int_0^\infty \frac{\cos(\omega x)}{x^m}dx &= V_0\omega^{-1+m}\int_0^\infty \frac{\cos(\omega x)d(\omega x)}{(\omega x)^m} \\ &= V_0\omega^{-1+m}\Gamma(1-m)\sin\frac{m\pi}{2}, \\ \frac{1}{C_p\omega} = V_0\int_0^\infty \frac{\sin(\omega x)}{x^m}dx &= V_0\omega^{-1+m}\int_0^\infty \frac{\sin(\omega x)d(\omega x)}{(\omega x)^m} \\ &= V_0\omega^{-1+m}\Gamma(1-m)\cos\frac{m\pi}{2}. \end{aligned}\right\} \quad (5)$$

$$\left.\begin{aligned} C_p &= \frac{\omega^{-m}}{V_0\Gamma(1-m)\cos\frac{m\pi}{2}}, \\ \tan\psi = C_p\omega R_p &= \tan\frac{m\pi}{2}, \\ \psi &= \frac{m\pi}{2}. \end{aligned}\right\} \quad \ldots\ldots \quad (6)$$

$\Gamma(1-m)$ is the Gamma function.

We conclude that when C_p varies as a power of ω, ψ is constant, and its value is given by equation (6).

Comparison with Experimental Data.

Relationships deduced by Warburg [1] and Krüger [3] in their theories are represented by equations (5) and (6) as special cases. The former has $m = 1/2$, $\psi = 45°$. The latter has $m = 1$, $\psi = 90°$.

The measurements made at Cornell gave constant values of m over a frequency range sufficiently extended to justify the application of equation (6). The results obtained by Wolff[6] may be considered first. He worked with five different cells, gold and platinum in diluted sulphuric acid of different concentrations. The values obtained for the polarization capacity are shown in logarithmic plot in fig. 5 of his paper. The curves are practically straight lines at the low frequencies over which range the phase angle ψ, also plotted in fig. 5, is, furthermore, nearly constant. The values of m in our Table I. are obtained from this straight portion of Wolff's curves for the polarization capacity. The values listed under ψ (calculated) are obtained by equation (6), while under ψ (observed) the values found for ψ at low frequencies are

TABLE I.

Application of equation (6) to measurements by Wolff[6].

Experiment No.	m.	Value of phase angle ψ.	
		Observed.	Calculated.
2	·19	17·5°	17·4°
3	·32	28°	29·2°
4	·15	14°	13·5°
5	·12	11·5°	10·7°
6	·24	21°	22·0°

listed. The agreement is very satisfactory. At the upper end of the range of frequencies used, Wolff finds that m and ψ increase, m for most of the electrodes reaching a value of nearly 1/2. The work of Jolliffe[5], done previously in the same laboratory, shows what happens at still higher frequencies. For gold in sulphuric acid of different concentrations he finds m and ψ to be constant, m being equal to 1/2, while the value of ψ, in different cells, lies between 33° and 40°. The experimental value of ψ is smaller than the value $\psi=45°$, derived from equation (6), using $m=1/2$. For gold Wolff has only one set of measurements and both m and ψ are still increasing at the upper end of his experimental range of frequencies, which stops where that of Jolliffe begins. In Wolff's work m reaches a value of ·33, ψ a value of 30°, this value of ψ agreeing well with the value $\psi=29·7°$ derived from equation (6) with $m=·33$. Considering the

fact that the results obtained with electrodes of different samples of the same metal often differ considerably, Jolliffe's results for gold cannot be regarded as inconsistent with those of Wolff. However, in view of the experimental difficulties involved in measuring accurately the polarization resistance at these high frequencies, experimental verification of Jolliffe's results should be awaited before concluding that equation (6) does not apply. The uncertainty regarding Jolliffe's work is deepened when we consider his data for platinum. For this metal he finds that m increases beyond 1/2 at the highest frequencies, while ψ decreases with increasing frequency, turning negative at the highest frequencies. This behaviour of ψ seems unlikely theoretically, and also, there is no indication of decreasing values of ψ in Wolff's work with platinum.

Consider the investigations of irreversible electrodes which are on record, other than those carried out at Cornell. All these investigations are made over comparatively narrow ranges of frequency and with an experimental accuracy which can be expected to be only moderate. In some cases m is found to be constant, in others it is not. There is no theoretical necessity that equation (6) should hold with exactness even when m is found to be constant, since the range of frequency employed is always comparatively narrow. Nevertheless, a survey of the experimental material shows that this equation, as a general rule, holds surprisingly well. As a matter of fact, the difference between theoretical and observed values is probably in every case within the limits set by the value of the experimental error. Typical instances are shown in Table II. In explanation of this table, it may be noted that when measurements were made at more than two frequencies and m and ψ are not constant, the values stated in the table are the average values over the complete frequency range employed. When more than one series of experiments were made with a certain electrolytic cell, but are not all included in the table, the references indicate which experiments are used.

When an electric current passes through a living tissue a polarization is produced similar in its frequency dependence to the polarization observed at irreversible metal electrodes. The polarization capacity varies inversely as a power of the frequency over a wide frequency range, with the exponent m usually around ·30. At low frequencies m decreases. Measurements which I have made [13] on a number of different tissues furnish results which are in good agreement with equation (6). However, it should be noted that the polari-

TABLE II.

Application of equation (6) to measurements of different irreversible electrodes.

Electrolytic cell.		Frequency range (cycles/second).	m.	ψ in degrees.		Author.
Metal.	Aqueous solution of			Obs.	Calc.	
Platinum	Sodium chloride	64–256	·06	6·5	5·5	Wien[10], p. 47.
Nickel	,, ,,	64–256	·10	9·0	9·0	,, p. 48.
Silver.....	,, ,,	64–256	·13	16	12	,, pp. 47 and 48.
Platinum	Sulphuric acid	500–7000	·19	17	17	Wolff[6], fig. 5, curve 2.
Gold	,, ,,	200–3000	·24	21	22	,, ,, ,, 6.
Platinum	,, ,,	700–7000	·32	28	29	,, ,, ,, 3.
Platinum black	,, ,,	64–256	·34	26	30	Wien[12], p. 381.
Gold	,, ,,	11000–2100000	·50	37	45	Jolliffe[5].
,, ...	,, ,,	645–2581	·48	41	43	Zimmerman[8].
Platinum	,, ,,	645–2581	·60	46	54	,,
Gold	Potassium chloride	570–3500	·62*	66	56	Miller[11].
Palladium black (saturated with hydrogen)	Sulphuric acid	64–256	·87	70	78	Wien[12], p. 396.

* In forming this average value, one experiment was disregarded, giving $m = ·22$, which is completely out of line with the values obtained in the other experiments and therefore assumed to be in error.

zation originates at the numerous surfaces of the cells of the tissue. In order to obtain values which may be considered to represent the polarization capacity C_p, and the phase angle ψ, of a single surface, a calculation has to be gone through which, due to the complexity of the material, is approximate only. For this reason this material is not so suitable for a strict verification of the theory.

Generally, equations (3) and (4) have to be solved by mechanical means. The application of these equations to experimental data will be considered in another place. Measurements of C_p and ψ of higher accuracy and over a more extended range of frequencies than exist to-day are, however, highly desirable.

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XXXIV. *A Direct Method of measuring the Velocity of Sound in Paper.* *By* D. A. Oliver, *B.Sc.**

Abstract.

An easily applied method of measuring directly the velocity of propagation of sound in a strip of paper is described, whereby the paper is fixed into a vibrating clamp and the resonant frequencies observed for various lengths of overhang. The validity of the method was checked by ascertaining for a phosphor bronze strip the value of $\sqrt{E/\rho}$ statically, and dynamically by the present method, and satisfactory agreement was found. Measurements on two kinds of paper are given in detail and comparisons carried out with static determinations. It is concluded that a representative value

* Communicated by C. C. Paterson, M.I.E.E.

for the velocity of sound in paper is $2{\cdot}1 \times 10^5$ cm./second, but tests on individual samples are desirable when this constant needs to be known with a precision of greater than 20 per cent.

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1. *Introduction.*

IN connexion with a larger investigation into the vibrations of loud speaker diaphragms, a knowledge of the velocity of propagation of sound in various grades of paper was desirable. As a direct determination of this physical constant does not appear to have been made previously, an easily applied method was developed which is outlined in this paper, and some typical results are described.

2. *Theory of Method.*

The velocity of propagation of sound c in a material is defined by the equation

$$c^2 = \mathrm{E}/\rho \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where c is the velocity in cm./second, E is Young's Modulus in dyne/cm.^{2} and ρ is its density in gm./cm.^{3} In the case of a simple homogeneous material it would appear sufficient to measure E and ρ separately and to calculate the value of c. For steel it is known that such a procedure gives a result correct to a few parts in a thousand, but in the case of paper it was found that while a static determination of E could be carried out, the density ρ was as difficult to measure precisely as to define, and therefore it was decided to measure the effective value of E/ρ directly, under dynamical conditions.

The method adopted consisted in vibrating a small strip of paper, clamped as a cantilever, and observing the frequency of resonance at which the amplitude of vibration was a maximum. The frequency for resonant vibrations of a simple cantilever, neglecting rotatory inertia, is derived from the well known general differential equation [1]

$$\frac{\partial^4 y}{\partial x^4} + \frac{m}{\mathrm{EI}} \frac{\partial^2 y}{\partial t^2} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which y represents lateral displacements, x the longitudinal coordinate, t the time, m the mass per unit length, E the value of Young's Modulus for the material, I the second moment of area of the section. The general solution of

equation 2 when the lateral displacement is a harmonic function of the time $y = a \cos(\omega t + \phi)$ is

$$v = (A \cosh qx + B \sinh qx + C \cos qx + D \sin qx) \cos(\omega t + \phi) \quad (3)$$

in which $$q^4 = m\omega^2/EI \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Inserting the boundary conditions for a cantilever and solving, it is found that for the fundamental mode of vibration in a horizontal plane

$$q = 0{\cdot}5969\pi/l \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Substituting this value for q in equation (4) and remembering that for a uniform cantilever of density ρ, width b and depth d, $m = \rho bd$ and $I = \frac{1}{12} bd^3$, we find that f the frequency for resonance is given by the equation

$$f = 0{\cdot}162 \frac{d}{l^2} \sqrt{\frac{E}{\rho}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

which is a simple function of the dimensions of the cantilever and the desired velocity of propagation of sound in the material. If for various lengths we find corresponding values of f and l, then a straight line through the origin should be obtained by plotting f to a base of $1/l^2$. Calling the slope of this line $\tan \psi$, we have

$$c = \sqrt{E/\rho} = \tan \psi / 0{\cdot}162\, d \quad . \quad . \quad . \quad . \quad (7)$$

This formula applies strictly when the cantilever is vibrated with its length in the horizontal plane and its width in the vertical plane.

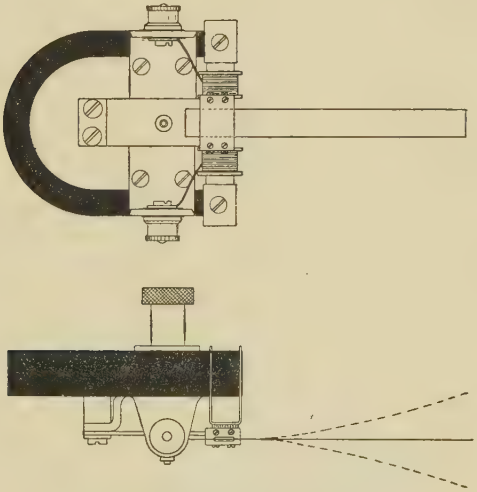
3. *Experimental Procedure.*

The paper cantilever was fixed to a vibrator and set into forced vibration in a similar way to the reeds in Frahm's frequency meter [2]. The frequency was observed at which the sharp maximum amplitude of vibration occurred when the vibrator was supplied with approximately constant current over the band of frequency embracing the main response of the cantilever.

To the end of a reed loud speaker movement—a G. E. C. Stork unit—was attached a brass clamp of the form shown in fig. 1. The clamping faces were slightly channelled out transversely to ensure definiteness at the point where the paper left the clamp itself. In the apparatus used by the author the first natural frequency of the vibrator reed was about 800 cycles per second and due to the lightness of the paper and the remoteness of its own natural frequency (about

50 cycles per second) no complications due to coupled vibrating systems arose. The values of current employed for the tests ranged from about 100 to 200 milliamperes and the source of power was a small variable frequency alternator. The frequency was varied by smooth rheostatic control and a range of 20 to 60 cycles per second could be obtained. A separately calibrated frequency meter of Wild's type was used to measure the individual resonant frequencies and this instrument gave all the necessary accuracy. Its calibration at a suitable constant input voltage was carried

Fig. 1.



Elevation and plan of vibrator.

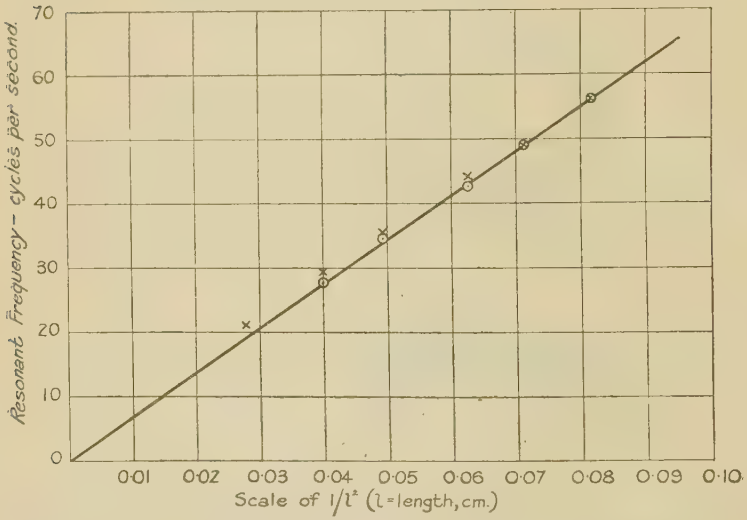
out and its error with applied voltage for the 50 cycles per second reading was ascertained. Both sets of errors were found small and were allowed for when necessary.

The general procedure was to test a given parallel strip of paper not more than 1 cm. wide at various known free lengths of overhang; preliminary tests indicating the approximate extreme lengths required to resonate at the two limits of the conveniently measured frequency range. After marking off in fine pencil lines from the squarely cut free end of the strip, the longest lengths were tested first and, if necessary, a small amount cut off each time the cantilever was reclamped in a new position.

Thickness measurements were made by micrometer screw gauge and by a special dial type indicator with two light spring jaws. The micrometer readings generally agreed very well with the indicator except in the case of very soft papers when they were usually a little less. In such cases the uncertainty in the thickness measurement largely decided the absolute accuracy of the final result.

It may be mentioned that vibration forms other than that of the simple fundamental deflexion form were obtained under certain conditions by raising the frequency of excitation. A number of these were examined quali-

Fig. 2.



Phosphor bronze cantilever results. (⊙ width 0·2 cm., × width 1·0 cm.)

tatively, but no attempt was made to correlate the frequencies at which they occurred.

4. *Experimental Check on Method.*

In order to verify equation (7) and to check that in actual fact the natural frequency was independent of the width of the cantilever, a uniform piece of phosphor bronze strip was taken and tested. The results obtained are shown in fig. 2 where the observed frequencies for resonance of the cantilever are plotted to a base of the reciprocal of the square of the length. The simple theory is confirmed for a width of 0·2 cm., but a similar series of measurements for a width of

1 cm. shows a consistent slight departure at the lowest frequencies. The results, however, merge into those obtained for the 0·2 cm. width at the higher frequencies as is seen in fig. 2.

As the composition of the phosphor bronze used in this experiment was unknown, the value of Young's Modulus was determined separately by deflecting the cantilever statically by known weights at its end and noting the deflection by a measuring microscope [3]. A linear relation between force and deflection was obtained from which the value of Young's Modulus was deduced. The density was not expected to vary much from sample to sample and a value, therefore, was taken from tables. The results are given in Table I.

TABLE I.

Results for Phosphor Bronze Cantilever.

Thickness	$1{\cdot}42\times10^{-2}$ cm.	
Tan ψ	$6{\cdot}9\times10^{2}$.	
E (static)...	$6{\cdot}8\times10^{11}$ dyne/cm.^{2}	(Measured).
ρ	8·8 gm./cm.^{3}	(Assumed).
$\sqrt{\frac{E}{\rho}}$ (dynamic value)	$3{\cdot}00\times10^{5}$ cm./sec.	(Measured).
$\sqrt{\frac{E}{\rho}}$ (static value)	$2{\cdot}8\times10^{5}$ cm./sec.	(Check Value).

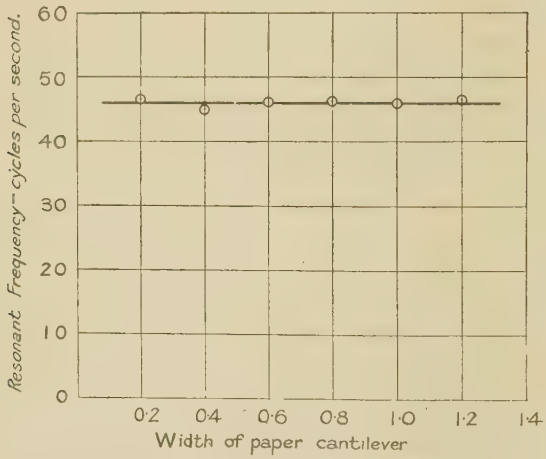
The discrepancy between the dynamically and statically observed values of $\sqrt{\frac{E}{\rho}}$ is a little greater than 5 per cent., of which the former is the more accurate. When the limitations on the various possible errors, such as those on thickness, are examined, this result must be regarded as a satisfactory check on the method, especially as it was considered at the time unnecessary to make a direct measurement of the density.

5. *Typical Results.*

Preliminary measurements were made on a certain grade of white Bristol board paper and the effect of the width of the cantilever employed was investigated. In fig. 3 is given a series of observations for cantilevers 5·70 cm. long and of various widths between the limits of 0·2 and 1·2 cm. It is seen that within the limits of experimental error, the

frequency is independent of the width. No effect such as is recorded in fig. 2 for phosphor bronze was found present with this paper and therefore a value of 1 cm. was adopted as the standard width to give a good average result for the material under test. The thinnest grade of white Bristol board is a paper which is homogeneous and uniform in thickness and was, therefore, chosen for the first series of measurements. Two strips 1 cm. wide were cut from the main sheet in directions mutually at right angles and carefully tested. The final observations are given in fig. 4, in which it is seen that the two sets of results are coincident, and reveal no inconsistencies among

Fig. 3.



Results showing resonant frequency independent of width.

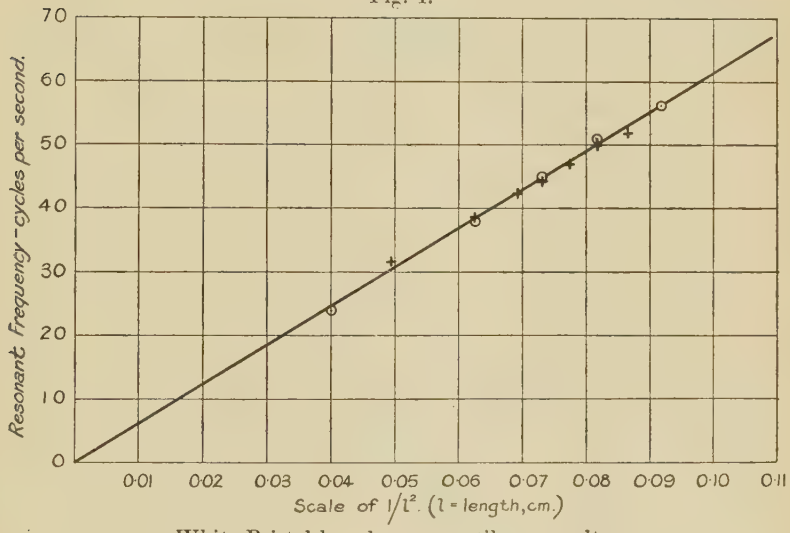
the two samples. The value of c calculated from the slope of fig. 4 is given in Table II.

Another series of measurements was made on a thicker and less uniform variety of brown corrugated paper specially made for loud speaker cones. Two strips were cut from a sample sheet and tested as before, and these gave the two curves in fig. 5 for which the slopes vary by as much as 50 per cent. for paper of nominally the same thickness and texture. These results are quoted by way of example and show why an error on the final result of perhaps 5 per cent. is not a serious matter in the light of variations in the material under test : especially in the extreme cases of rough or corrugated papers which do not lend themselves to

precision measurement, as the main difficulty is to evlauate the effective thicknesses sufficiently accurately.

In the case of the white Bristol board paper the mean of ten thickness measurements was $0{\cdot}017_{3\pm7}$ cm. and the mean of two such mean values on two samples from the same sheet gave a value of $0{\cdot}017_0$ cm. On the other hand, fourteen

Fig. 4.



White Bristol board paper cantilever results.

TABLE II.

Results for Paper Cantilevers.

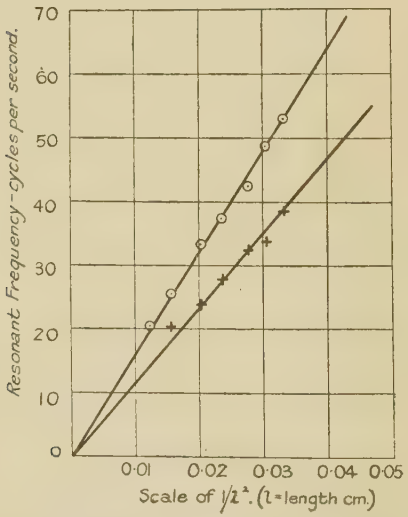
Material.	Tan ψ.	Thickness cm.	$\sqrt{\frac{E}{\rho}}$ cm./sec.
White Bristol board paper	$6{\cdot}13\times10^2$	0·0173	$2{\cdot}18\times10^5$.
Brown corrugated paper	$1{\cdot}60\times10^3$ $1{\cdot}17\times10^3$	0·047	$2{\cdot}1\times10^5$. $1{\cdot}5\times10^5$. [$1{\cdot}8\times10^5$ (mean)].

thickness measurements on the brown corrugated diaphragm paper gave a mean thickness of $0{\cdot}047_{0\pm50}$ cm., or a possible variation of 10 per cent. from the mean value. It is clear therefore that in most instances the accuracy of the thickness measurement largely determines the accuracy of the final value of c. The results are summarized in Table II.

It was considered of interest to check the dynamically obtained result on the white Bristol board paper by measuring the values of E and ρ directly. The force-deflexion curve for small masses attached at a distance L of 3·4 cm. from the clamp is given in fig. 6 and the inverse of the slope $\Delta y/\Delta w$ is used in the following equation to derive the value of Young's Modulus E.

$$E = \frac{4L^3 g}{bd^3}\left(\frac{\Delta w}{\Delta y}\right) \text{ dyne/cm.}^2 \quad . \quad . \quad . \quad . \quad (8)$$

Fig. 5.



Brown corrugated paper cantilever results.

where L = distance in cm. from clamp of weight w gm.

y = deflexion at distance L cm.

b = width of paper cantilever, cm.

d = thickness, cm.

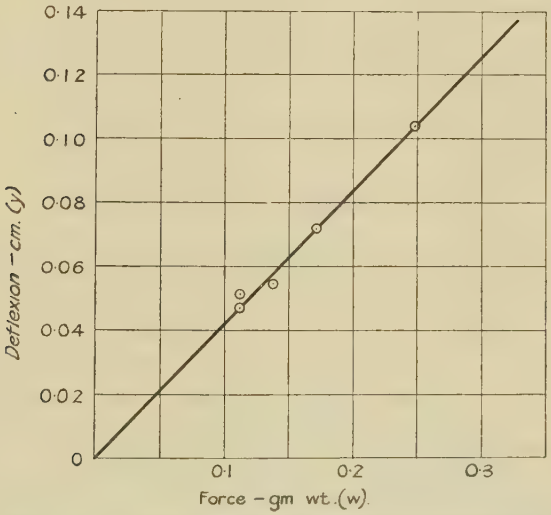
g = 981 cm./sec.^{2}

From fig. 6 $(\Delta w/\Delta y)$ is 2·38 gm./cm. and on substitution $E = 7{\cdot}1 \times 10^{10}$ dyne/cm.^{2} It has already been pointed out that the density ρ is as difficult to measure as to define but by using the same value of the thickness d as in equation (8), and measuring directly the mass per unit area of the paper,

a value of $\rho = 1{\cdot}2_1$ gm./cm.^{3} was obtained. The statically deduced value of $\sqrt{\frac{E}{\rho}}$, on this basis, is found to be $2{\cdot}4 \times 10^5$ cm./sec. which is in reasonable agreement with the more accurate and directly observed result $2{\cdot}1_8 \times 10^5$ cm./sec.

McLachlan [4] has measured Young's Modulus for paper by plotting a load extension diagram for strips of paper in tension. His values of E for different papers vary from $1{\cdot}9 \times 10^{10}$ to $4{\cdot}6 \times 10^{10}$ dyne/cm.^{2} and the corresponding values of ρ, obtained as already described, fall between the

Fig. 6.



Determination of Young's Modulus by static deflection of paper cantilever.

limits of 0·6 and 0·8 gm./cm.^{3} The calculated values of c, corresponding to the measured static values, range between $1{\cdot}7 \times 10^5$ cm./sec. and $2{\cdot}4 \times 10^5$ cm./sec. which agree very well with the dynamical observations recorded in this paper. Caplet [5] for a certain drawing paper ($\rho = 1{\cdot}07$) quotes a value of $2{\cdot}3 \times 10^5$ cm./sec. for longitudinal propagation. The conclusion appears to be, therefore, that the statically and dynamically observed results are in good general agreement with one another and that a velocity of propagation of sound of $2{\cdot}1 \times 10^5$ cm./sec. can be taken as a representative figure for paper, but where greater accuracy is desired individual observations on particular samples must be made.

Acknowledgment.

This investigation was carried out in the Electrical Research Laboratory at the Northampton Polytechnic and was only possible through the kindness of Mr. A. C. Jolley, F.Inst.P. The Author's best thanks are due to him, not only for the facilities provided, but also for his interest and encouragement during the progress of the work.

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(1) *E. g.* Lamb, "Dynamical Theory of Sound," p. 126 (1925).
(2) Drysdale and Jolley, Elec. Meas. Inst. ii. p. 221.
(3) Drysdale and Jolley, Elec. Meas. Inst. ii. p. 223.
(4) McLachlan, Phil. Mag. xiii. p. 115 (1932).
(5) Caplet, *Assoc. Franç. pour l'Av. des Sci.* 53rd Session, pp. 242–244. (Abs. E. W. and W. E. viii. p. 215 (1931).

XXXV. *Notices respecting New Books.*

A Treatise on Physical Chemistry: A Co-operative Effort by a Group of Physical Chemists. Second edition, edited by H. S. Taylor. [Vol. I., pp. 852; Vol. II., pp. 866.] (London: Macmillan and Co., 1932. Price 30*s.* each.)

RECENT advances in various branches of physical chemistry have led Professor Taylor to undertake a thorough revision of some of the chapters in his well-known work. As a result the page total has increased from 1260 to 1720, and this is largely the result of the expansion of particular sections.

The chapters dealing with the kinetic theory of the gaseous and liquid states have been entirely rewritten by new authors with vastly improved results, and, in accordance with the considerable developments which have occurred in the application of the quantum theory to physico-chemical problems, S. Dushman has greatly expanded the section devoted to this subject. Colloid chemistry is also represented by a new author (Dr. E. O. Kraemer), and the result is a well-balanced account of the modern aspects of this rapidly expanding branch of physical chemistry. The chapters devoted to the electrochemistry of solutions and reaction velocities in homogeneous and heterogeneous systems also show marked signs of revision.

The general result of the alterations is to add very much to the value of the treatise in accordance with the original plan of incorporating the specialised knowledge of a number of experts. As was the case in the original volumes, the different sections in

the new edition do not by any means reach the same standard of merit.

To preserve approximate equality of size in the two volumes, the chapter on the electro-chemistry of solutions has been transposed from the second to the first volume. This is rather unfortunate in view of the specialised thermodynamic treatment of the subject. The space occupied by this could with advantage have been considerably reduced.

The chapter on conductance and ionization preserves its value as a source of original references, and revision has added but little in the way of recent developments.

The modifications in the chapter on reaction velocity in homogeneous systems represent an improvement on the original, but this section lacks balance and breadth of view, and a fundamental revision is required for the attainment of the high level of excellence which is characteristic of many other sections.

In a treatise on physical chemistry of the scope and standing represented by the two volumes under review it is somewhat surprising to find that important topics such as dipole moments, the parachor, and the catalytic action of acids and bases are either not at all or very inadequately dealt with. It may be that such omissions are in some measure to be ascribed to the circumstance that the majority of the authors envisage the developments of physical chemistry through American spectacles.

Genetic Principles in Medicine and Social Science. By Lancelot Hogben. [Pp. 230.] (London: Williams & Norgate, Ltd., 1931. Price 15*s.* net.)

Professor Hogben's stated object in writing this book is to indicate the nature of the methods of the human geneticist and to demonstrate the use which can be made of the materials of human pathology. He considers that human genetics is about to become an exact science, and that it is wise to refrain from speculation in regard to the effects of different factors in moulding the future race or individual. He frankly avoids the use of the word "eugenics," maintaining it is associated with a biased viewpoint and with partial observers.

The first half of the book is a quantitative critical discussion of data drawn from studies on twins, blood-groups, and certain "hereditary" diseases (hæmophilia, night blindness). The evidence of the application of Mendel's law to humans and its relation to the modern knowledge as to the chromosome splitting is considered and analyzed mathematically. Emphasis is laid upon the difference between the effects of nature (the gene) and of nurture (environmental conditions) upon the individual, the family, and the race. The methods used in making this distinction are embodied in the first portion of the book.

In the second half of the book the problems of racial characteristics, population changes, birth-rate rise and fall, and such modern factors as birth-control and sterilization are considered. The mathematical methods of the first part are applied still further in the second part. Some of Professor Hogben's statements suggest that he is unconsciously biased as to the value of the methods he advocates and the value of certain inferences. It is very questionable whether "the goal of scientific enquiry is the representation of experimentally demonstrable data with the aid of mathematical symbolism." This is a legitimate means to an end—the correct comprehension of the mechanism of biological changes,—but it does not follow that a mathematical formula is an end in itself.

Again, on page 170 he quotes Bauer, Rischer, and Lenz as stating that the Chinese are racially disinclined for warfare, and appears to disagree with them on the grounds that recent events in China demonstrate otherwise. Yet only one person in five thousand is engaged in fighting—this surely is not a serious criticism of their contention.

The questions of birth-control and sterilization are very fully discussed, and certain popular modern views are heavily discounted. Three things might have been more fully mentioned: namely, the unknown reasons for the widespread fall in the Western birth-rate, the distinction between natural and artificial methods of birth-control, and the very important problem of the relation of the individual to the State. A book of this scope should discuss this fundamental matter, especially as the author is advocating certain remedial measures for the eradication of some of the conditions discussed. The whole question turns on the liberty of the individual and the rights of the State.

Professor Hogben has produced a very important book, which breaks new ground and establishes genetics as a weapon for attacking many medical and social problems. Whether it can be called a new science or merely another phase of applied biology is another matter.

An Introduction to the Mathematics of Map Projections. By R. K. Melluish, M.A. (Cambridge, 1931: at the University Press. Price 8*s.* 6*d.*)

This is a book for the student of geography who is interested in the mathematical theories which underlie the construction of maps. First of all the Author traces the history of the projections concerned. He then gives a good account of the general theory: the properties of the four main classes of projections are deduced as special cases of the general theory. After a chapter on the theory of the Indicatrix and the method of comparing one projection with another, he discusses the question of finite

measurements. He concludes with a discussion of the best projection for a given country and a discussion of the general problem of conformal representation.

This book, which is the first of its kind, will certainly be useful to the mathematically-minded student of geography. It is attractively written.

The Theory of Spherical and Ellipsoidal Harmonics. By E. W. Hobson, Sc.D., LL.D., F.R.S., Sadleirian Professor of Pure Mathematics in the University of Cambridge. (Cambridge, 1931: at the University Press. Price 37*s.* 6*d.*)

It is a great pleasure to welcome this important book. Since the foundations of the theory of Spherical Harmonics by Legendre and Laplace, these functions have been of first-class importance. Nevertheless, until the appearance of this work there has been no complete and exhaustive account available in English.

In the first four chapters the properties of the ordinary spherical harmonics are investigated. The treatment is novel in certain respects, and to the pure and applied mathematician alike it will be valuable and useful.

The general definitions of Legendre's associated functions of unrestricted degree, order, and argument are then given. The functions are treated as a special case of hypergeometric functions. Their asymptotic expressions follow: also the addition theorems; and in the next chapter a full discussion of the zeros of Legendre's functions and associated functions.

The next chapter has as its subject the harmonics for spaces bounded by surfaces of revolution.

Finally there is a very full treatment of ellipsoidal harmonics.

This work will be of the greatest value to pure mathematicians, who will appreciate the completeness of the treatment accorded to these important functions, especially in view of the fact that the properties of spheroidal, conal, toroidal, and other special functions have in general been treated as separate problems. The applied mathematician, who so often has to make use of the various functions, will find that his interests have also been considered.

The work, produced by the Cambridge University Press, is, of course, beautifully printed. But it is a pity that the paper is not more worthy of the text.

Kinetics of Homogeneous Gas Reactions. By Louis B. Kassel. [Pp. 307+xxi.] (The Chemical Catalog Company Inc., New York. Price $6.50.)

This volume is a notable addition to the well-known series of monographs published by the Chemical Catalog Company of New York, under the auspices of the American Chemical Society.

Dr. Kassel's presentation of what is, perhaps, the most interesting development of modern physical chemistry is eminently successful.

The fundamental theoretical problems connected with reactions in gases are dealt with from the point of view of statistical mechanics in the first half of the book. In the subsequent chapters, the results obtained in the theoretical section are considered in relation to experiment. The treatment of bimolecular and complex reactions is excellent, while the chapters on unimolecular reactions are particularly comprehensive. A critical attitude is maintained throughout, and, indeed, this is one of the most valuable features of the book, which is based very largely on experimental data established within the last ten years.

The style is rather formal, and the discussion often too detailed for the general reader. For this reason the book is likely to be of the greatest use to those who are actively engaged in the investigation of the subject. In this direction it satisfies a real need, and it may be accepted as an authoritative work which describes accurately and adequately the position which has been reached in this active field of research.

Partial Differential Equations of Mathematical Physics. By H. Bateman, Professor of Mathematics, Theoretical Physics and Aeronautics, California Institute of Technology, Pasadena, California. (Cambridge University Press, 1932. Price 42*s.*)

This is an immensely impressive work, which will be of great value to the student of applied mathematics and mathematical physics.

The book is concerned with the boundary problems of mathematical physics. The chief aim is to develop the exact analytical solutions. After an introductory chapter on the classical equations comes a chapter on the applications of the theorems of Stokes and Green. Chapter 3, on two dimensional problems, gives a full and interesting account of two dimensional problems, and is followed by a chapter on conformal representation. Three dimensional questions are then considered—in a chapter on polar coordinates, another on cylindricals, and others on ellipsoidal coordinates, paraboloidal and toroidal coordinates. In this part of the work there is some overlapping with Hobson's Spherical and Ellipsoidal Harmonics. Finally, there is a discussion of diffraction problems and a useful chapter on non-linear equations.

Throughout the book there are very full references. The examples, of which there are many, will also greatly add to its value.

XXXVI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

March 23rd, 1932.—Sir Thomas H. Holland, K.C.S.I., K.C.I.E., D.Sc., F.R.S., President, in the Chair.

THE following communication was read:—

'The Rocks between the Carboniferous and Trias in the Birmingham District.' By Prof. William S. Boulton, D.Sc., A.R.C.S., F.G.S.

The results obtained from a detailed study of the cores from deep borings at Windsor Street Gas Works in east Birmingham led the Author to re-investigate the rocks in the Midlands which link up the Carboniferous and Trias.

The succession at Windsor Street is continuous to a depth of over 1000 feet, and includes the Bunter (with a basal breccia), the Nechells Breccia, and part of the Calcareous Conglomerate Group.

The content of the breccias and conglomerates was described, and a graph was given showing the percentage distribution of rock types at different depths. The heavy mineral residues of the associated sandstones have also been determined.

The upper part of the Breccia Group, consisting of a coarse quartzite breccia, was shown to be of Bunter age, while the Nechells Breccia proper, 350 feet thick, consists of 70 to 80 per cent of Uriconian igneous rocks. The Bunter Breccia is separated from the Nechells Breccia by an abrupt lithological break, but without angular discordance. A similar, and perhaps stronger break, occurs at the base of the Nechells Breccia. A detailed examination of the cores of other borings shows that these features are maintained throughout an area of at least two square miles in eastern Birmingham.

All available data were collected, and a map was given showing the shape of the pre-Trias floor of the Birmingham district west of the Birmingham Fault.

Evidence was given to show that the Barr Beacon Beds underlying the Bunter Pebble Beds, and mapped by the Geological Survey as Hopwas Breccia, are of Bunter age, and with them were correlated the breccias at Tower Hill, near Hamstead, and also the more extensive beds of sand-rock at the base of the Bunter of Cannock Chase.

The content of the breccias of Hopwas, Sutton Park, Warley, Northfield, and the Lickey were dealt with and compared, and evidence was adduced to show that, though discontinuous deposits, they are of the same general age, and

have all been derived from highlands to the immediate east and south, whose outcrops mainly consisted of Uriconian felsite- and andesite-tuffs and lavas, and basalts.

Stress was laid on the extensive and prolonged erosion which accompanied and followed the Hercynian earth-movements in the area; the known Clent Beds (upper Enville Beds) must represent a small fraction of the deposits of this age, most of which lie concealed under newer beds in the Midlands. The Clent Beds are probably of the same age as some of the beds in the North of England, classed as Permian, which post-date the main Hercynian folding.

April 27th, 1932.—Sir Thomas H. Holland, K.C.S.I., K.C.I.E., D.Sc., F.R.S., President, in the Chair.

The following communication was read :—

'The Stratigraphy of the Valentian Rocks of Shropshire : the Longmynd-Shelve and Breidden Outcrops.' By Walter Frederick Whittard, Ph.D., A.R.C.S., D.I.C., F.G.S.

A dual division of the Valentian rocks of Shropshire into a lower group, the Pentamerus Beds, and an upper group, the Purple Shales, was adopted. Further, two lithological subdivisions of the Pentamerus Beds, the Arenaceous Phase and the Mudstone Phase, were recognized.

The Longmynd-Shelve outcrop is divided into several areas by glacial deposits. The rocks of these areas exhibit different lithological and faunal characters, due to the variable conditions under which they were laid down.

The faulting of the Longmynd-Shelve and Breidden outcrops was mentioned; the Church Stretton Main Fault (F1) received special treatment, because of the evidence which the Marshbrook outlier provided with regard to the throw of the fault.

The graptolites from the Upper Valentian rocks of Shropshire favoured a correlation of the shelly fauna with the *Monograptus turriculatus* and *Monograptus crispus* Zones of the Gala Group.

Two distinct faunas characterize the Valentian rocks of the main outcrop, and these were selected as the standard faunas. Several local modifications of each standard fauna are present in the Longmynd-Shelve and Breidden outcrops. The character of the sea-bed and the control it exerted on the kind of fauna which frequented a particular area were stressed, and attention was directed to the mud- and sand-loving genera and species.

The encroachment of the sea over the district in Upper Valentian times resulted in a complicated region of land and sea to which the name of 'Salopia' was given. Alongshire structures, such as characterize many subsiding coastlines, were

described from the Upper Valentian rocks. Remnants of the Valentian landscape are still preserved, and it is possible to reconstruct locally the configuration of the land.

May 11th, 1932.—Prof. W. W. Watts, LL.D., Sc.D., M.Sc., F.R.S., Vice-President, in the Chair.

Prof. William A. Bone, D.Sc., Ph.D., F.R.S., delivered a lecture on 'Some Recent Investigations on the Maturing and Chemical Constitution of Coal'.

The lecturer reviewed recent researches, and more particularly those carried out in his own laboratories upon the chemical constitution of coals and their maturing, including the causes and development of their coking propensities.

The importance of dealing with the problem as fundamentally one of organic chemistry was stressed, and the different lines of 'thermal', 'solvent', and 'chemical' attack were explained, together with the experimental methods involved. It was shown that mere ultimate analyses of the 'dry-ashless coal substances' have little significance apart from a knowledge of the inner chemical structure of coal.

It was shown, in the first place, how properly graded experiments upon the thermal decomposition of *dry* brown-coals have revealed the operation of their successive and independent chemical changes; namely, the elimination (i) of CO_2 and H_2O simultaneously as if by some internal 'condensation', (ii) of methane, higher paraffins, and olefines, as if by the splitting off of alkyl side-chains etc., and (iii) of hydrogen. The results of typical 'solvent-attacks' (and more particularly of pyridine and benzene, respectively) upon the coal substance were then discussed. The superiority of the benzene-pressure-extraction was explained, and its application to brown-coals, lignites, bituminous coals, etc. set forth in detail. The lecturer described how the coking propensities of bituminous coals can be ascribed to the presence or formation therein of certain chemical constituents which, there are strong grounds for believing, have originated in, and gradually developed from, the phenolic constituents of brown-coals. Also, that such 'coking constituents' are substantially absent from semi-bituminous coals and anthracites.

Finally, the chemical constitution of the main coal-substance (that is, of the 'residue' after the benzene-pressure-extraction) was discussed in the light of recent discoveries. It was shown that the C/H ratios of *all* such 'residues', whether from brown-coals, lignites, or bituminous coals, would suggest a 'benzenoid structure', and how this anticipation has been borne out by the discoveries in question.

Thus, it has been found that such coal 'residues' are completely oxidized by hot alkaline-permanganate solution to carbonic anhydride, acetic and oxalic acid, and a mixture of benzene-carboxylic acids, and that in each particular case a 'carbon-balance', showing its distribution among the various oxidation products, can be established experimentally such carbon-balances for typical coals of varying degrees of maturity were shown and discussed. The proportion of the original carbon finally appearing as benzene-carboxylic acids in the oxidation-products varies from about 30 up to 50 per cent (or more); but, owing to the nature of the oxidation-process, this by no means represents all the 'benzenoid' carbon in the original coal-substance.

The course of the oxidation would seem to be 'stage-wise'; possibly something as follows:—

Coal substance → { colloidal / humic acids } → { crystalline acids } → { acetic / oxalic / benzenoid } acids

plus carbonic anhydride at varying intermediate points; and, at one time or other, no less than ten out of the twelve possible benzene carboxylic acids have been isolated from among the oxidation products.

These researches have not only afforded the first unimpeachable quantitative evidence of the essential 'benzenoid' constitution of the main coal substance, but also established new experimental methods and technique for the exploration of the new field thereby opened; some of their implications were discussed.

So far as has been ascertained at present no benzenoid acids result when cellulose is similarly oxidized by means of hot alkaline permanganate, and the experiments are being extended to both lignin and peat, the latter of which has already shown some evidence of benzenoid structure. The question naturally arises as to whether coal has been so directly produced from ligno-celluloses as has usually been supposed hitherto, or whether it may have to be regarded as a synthetic product built up from the much simpler material into which lignin (with or without celluloses) is resolved during the 'peat-bog stage'.

Prof. Bone illustrated his lecture with lantern-slides and exhibited samples of carbon-balances for typical coals of varying degrees of maturity.

The Editors do not hold themselves responsible for the views expressed by their correspondents.